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F33615-74-C-1053

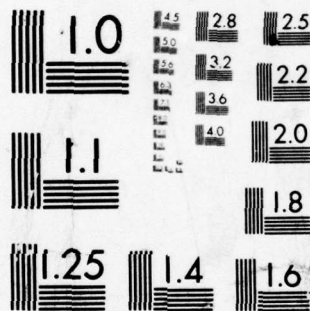
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## PHOTOGRAPHIC WASTE UTILIZATION

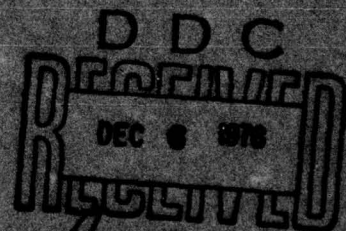
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OCTOBER 1978

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TECHNICAL REPORT AFAL-TR-78-163  
FINAL REPORT FOR PERIOD 1 OCTOBER 1978 - 2 FEBRUARY 1979

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19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFAL-TR-76-162	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) PHOTOGRAPHIC WASTE UTILIZATION.	5. TYPE OF REPORT & PERIOD COVERED Final Technical Report, 1 Oct 73-2 Feb 76	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Sandra S. Donovan	8. CONTRACT OR GRANT NUMBER(s) F33615-74-C-1053	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Horizons Incorporated Div. of Horizons Research Incorporated 23800 Mercantile Rd., Cleveland O., 44122	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS USAF0050	
11. CONTROLLING OFFICE NAME AND ADDRESS United States Air Force Air Force Systems Command, HQ 49th Test Wing, Wright-Patterson AFB, Ohio	12. REPORT DATE Oct 76	13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (If different from Controlling Office) Air Force Avionics Laboratory Air Force Wright Aeronautical Laboratories Air Force Systems Command Wright-Patterson Air Force Base, O., 45433	15. SECURITY CLASS. (of this report) Unclassified	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.  12 6pp.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Cold-setting ceramic foam      Safe disposal Insulating castable      Ultramarine pigments Insulating firebrick      On-site ceramic foam preparation Photographic processing wastes      Waste recycling		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objective of this program was to incorporate photographic processing wastes into a useful product, or to render the wastes harmless for a Class 3 landfill. The wastes were incorporated into a cold-setting ceramic foam, a ceramic castable, and an ultramarine pigment. Technical and economic evaluations indicated the foams might possibly be used for insulating firebricks up to 2000°F, and sold at a profit; the castables could be used		

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→ as an insulating castable up to 2000°F, but probably not sold at a profit; and the pigments could be made, but not profitably. From environmental exposure tests, for safe photowaste disposal in a Class 3 landfill, the 1000°F cured, clay-containing foam (preferred) or the room temperature cured, nonclay-containing foam, appear suitable as long as the landfill is not excessively alkaline. For excessively alkaline landfills, a 1000°F cured clay-containing castable appears suitable. The recommended level of photowaste incorporation is 10-20% by weight of green ceramic.



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## PREFACE

Photographic Waste Utilization was studied under Air Force Contract F33615-74-C-1053. The objective was to incorporate photographic processing wastes into a useful product, or to render the wastes harmless for a Class 3 landfill.



SUMMARY

The original contract had as its objective the elimination of pollution hazards associated with disposal of photographic processing wastes at a projected rate of 10 tons per week. To this end, work was done to incorporate photowaste into a ceramic foam, a ceramic castable, and to modify it to an ultramarine pigment. All three approaches showed technical feasibility and varying levels of technical success, but pigment fabrication was deemed economically unfeasible.

The amended contract had as its objective economic disposal of photowaste material either by its incorporation into a useful product or by its being rendered harmless and suitable for a class 3 landfill. Accordingly, two odorless products have been made and a means of safe disposal has been specified.

These two products are a ceramic foam capable of use as an insulating firebrick and a ceramic castable, capable of use as an insulating castable. Each green product contains about 10% by weight of photowaste. For the properties we tested, our products were about identical or somewhat better than comparable commercial products. From our approximate cost figures, the foam possibly might be sold at a profit, but not the castable. The manufacturing costs for the foam are estimated at 23.6 cents per pound, and for the castable at 25.5 cents per pound. Capital equipment and a functional plant layout for these products are given. Also detailed is a portable unit for on-site foam fabrication in a wide range of climates. However, this unit presumes a knowledge on the part of the user of how to substitute on-site materials as fillers.

From the environmental exposure tests, for safe photowaste disposal in a class 3 landfill, the 1000°F cured, clay-containing foam (preferred) or the room temperature cured, non-clay-containing foam appear suitable as long as the landfill is not excessively alkaline. For excessively alkaline landfills, a 1000°F cured castable appears suitable. The recommended level of photowaste incorporation is 10-20% by weight of the green ceramic.

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SECTION I  
INTRODUCTION

The photographic waste derived from spent black and white photographic solutions consists of a wide variety of chemicals. The major constituents are sodium thiosulfate and sodium sulfite, with minor constituents of sulfate, carbon, carbonate, aluminum, boron, potassium, chloride, and various other metals. About 10 tons of this waste material - a combination of developer and fixer - was anticipated each week from the Air Force photographic processing facilities, and its safe disposal [Ref. 1, 2] was seen as a problem.

SECTION II  
PROGRAM OBJECTIVE

The research program which began October 1, 1973 had as its original objective safe disposal of photographic wastes by incorporation into a useful product. The principal products to be considered were cold-setting ceramic foams. For the amended contract which began February 3, 1975, the objective was to economically dispose of the waste material either by its incorporation into a useful product or by its being rendered harmless and suitable for a class 3 landfill.

SECTION III  
METHODOLOGY

The methodology and results for the original and for the amended contract will be discussed separately.

- 
1. R. E. Lotz, Chemical Wastes Generated by Air Force Photographic Operations, Air Force Weapons Lab., Kirtland AFB, New Mexico, September 1972, AD 750 552.
  2. E. E. Lefebure and R. A. Callahan, Toxic Effects of Color Photographic Processing Wastes on Biological Systems, Environmental Health Lab., Kelly AFB, Texas, August 1970, AD 753 663.

1. Original Contract (October 1, 1973 - September 30, 1974)  
Methodology

a. Product Objectives

The major thrust of the program was to seek methods and means which would permit encapsulation of the material into a monolithic matrix bonded by aluminum phosphate hydrate in a low cost, laboratory scale process, capable of large quantity scale-up and throughput. Horizons has experience in the preparation of cold-setting foams [Ref. 3, 4, 5, 6]. The foamed structures have wide application possibilities because of their simplicity of formation, and range of available densities and properties. The principle of foam fabrication is quite simple. A liquid acid phosphate component is combined with a powdered basic component such that the neutralization reaction completes the formation of glassy phosphate binder material. The heat liberated by the neutralization reaction aids the gas-forming agent to generate gas which is trapped within the mixture and causes it to foam. The ratio of the liquid to solid component controls the pore size and cure rate. Cure rates as low as a few minutes are easily obtained.

The foam can be made by using numerous different components and fillers. The acid component can be an aqueous solution of an aluminum, calcium, or zirconium phosphate, with an excess of phosphoric acid present. The acid component can be made by combining the oxides, hydroxides, carbonates, acetates, or silicates of aluminum (preferred), zirconium, or calcium with  $P_2O_5$  and water within the following proportions:

1 mole $Al_2O_3$ :	Between 2 to 5 moles $P_2O_5$
1 mole $ZrO_2$ :	From 1 to 3 moles $P_2O_5$
1 mole $CaO$ :	Between 0.6 and 3 moles $P_2O_5$
1 mole $P_2O_5$ :	Between 5 and 15 moles $H_2O$

- 
3. What's Happening with Foamed Ceramics, Ceramic Age, November 1969.
  4. J. Magder, Foamed Ceramics, U. S. Patent 3,330,675, July 1967.
  5. R. W. Sicka, Foamed Ceramics, U. S. Patent 3,625,723, December 1971.
  6. M. S. Vukasovich and H. L. Johns, U. S. Patent 3,148,996, September 1964.



to obtain an acid component solution with a viscosity of 800 to 6000 centipoises at 72°F.

The basic component can be selected from the oxide, hydroxide, silicate, or carbonate of calcium, magnesium, zirconium, strontium, barium, aluminum, lithium, iron, and zinc. The photowaste is mixed with this basic component. The amount of powdered basic component added to the acid component must neutralize its excess acid.

The gas-forming agent can be a carbonate of calcium, magnesium, strontium, barium, lithium, ammonium, or iron; metals such as aluminum, magnesium, zinc, or iron, each of which liberates hydrogen when treated with phosphoric acid; compressed or liquified gases such as compressed air, nitrogen, carbon dioxide, trichloromonofluoromethane, dichlorodifluoromethane; or readily decomposable compounds such as hydrogen peroxide, or ammonium nitrite. Certain of the above gas-forming agents also can serve to neutralize the excess phosphoric acid.

The preferred acid component contained phosphoric acid, aluminum oxide, and magnesium oxide. The preferred basic component contained calcium, silicate, aluminum, magnesium, and iron oxides plus a magnesium carbonate foaming agent. The rationale will be discussed in detail later. The aluminum phosphate binders have been the subject of extensive study and application [Ref. 5, 6, 7, 8, 9]. The background of phosphate reactions with metal oxide materials is covered in the excellent reviews of Kingery [Ref. 10, 11, 12, 13]. Thermal treatment of

7. H. H. Greger, Phosphate Cements, U. S. Patent 2,450,952.
8. H. H. Greger, Solid Aluminum Hydrogen Phosphates, U. S. Patent 2,538,867.
9. H. H. Greger, Method of Preparing a Mineral Binder, U. S. Patent 2,455,758.
10. W. D. Kingery, Fundamental Study of Phosphate Bonding in Refractories: I. Literature Review, J. of Amer. Ceramic Soc. 33, 239-241 (1950).
11. *ibid.* II. Cold-Setting Properties, *loc. cit.* 242-247 (1950).
12. *ibid.* III. Phosphate Adsorption by Clay and Bond Migration, *loc. cit.* 247-250 (1950).
13. *ibid.* IV. Motors Bonded with Monoaluminum and Monomagnesium Phosphate, J. Amer. Ceramic Soc. 35, 61-63 (1952).

aluminum phosphate bonded materials causes complex solid state crystallographic transformations to occur over the thermal range required for service [Ref. 14, 15, 16, 17, 18, 19]. For this reason, firing of the foam is suggested for all high temperature applications.

Two minor efforts were to (1) incorporate the wastes into a ceramic castable, and (2) produce ultramarine pigments.

To fabricate the castable, a liquid sodium silicate solution is combined with powdered mineral oxides like aluminum, calcium and magnesium oxide plus the photowaste, and cured at whatever temperature is desired up to about 2000°F. Generally the higher the temperature the stronger the castable. The N-type sodium silicate solutions can range from about 25 to 50% by weight of the total mix, with the powder being about 25% by weight of the mix.

- 
14. I. L. Rashkovan, L. N. Kuzminskaya and V. A. Kopiekan, Thermal Transformations in the Aluminum Phosphate Binding Agent, *Izvestiya Akademii Nauk SSR, Neorg. Materialy* 2, pg. 541-549 (1966).
  15. V. M. Mcdvedava, A. A. Medvedev, and I. V. Tananaev, Investigation of the Thermal Transforamtions in An Alumina-phosphate Binder by the Methods of Infrared and X-Ray Diffraction Study, *Isvestiya Akademii Nauk SSR, Neorg. Materialy* 1, pg. 211-217 (1965).
  16. Ya. V. Khyucharev and L. I. Skoblo, Composition of the Products Formed by the Hardening of Aluminum Phosphate Binder in Refractory Corundum Compositions, *Zhurnal Prikladnoi Khimii* 38, pg. 520-526 (1965).
  17. M. F. D'Yvoire, Sur des phosphates d'aluminum du groupe  $P_2O_5/Al_2O_3 = 2$ , *Compt. rend.* 247, 297-300 (1958).  
M. F. D'Yvoire, Evolution thermique de phosphate d'aluminum du groupe  $P_2O_5/Al_2O_3 = 3$ , *Compt. rend.* 245, 531-534 (1957).  
M. F. D'Yvoire, *Bull. Soc. Chim. France* 145, 2277, 2283 (1960).
  18. W. R. Beck, Crystallographic Inversions of the Aluminum Orthophosphate Polymorphs and Their Relation to Silica, *J. Amer. Cer. Soc.* 32, pg. 147 (1949).
  19. K. Wen-min, N. Tchang-ti- and H. Wenter, Phase Transformation of Aluminum Phosphate Adhesive at 105-500°C, *Guisuanyan Xuebao*, pg. 65 (1964) CA 61:15808.

To make the ultramarine pigment, the photowaste plus clay is combined with sodium silicate.

b. Synthetic Photowaste

Since the actual photowastes were not available, three different model photowastes were used in the preparation of the foams, castables, and pigments. The first two which were used for the foam preparation were pure sodium thiosulfate, and the residue recovered from distilling a used black and white fixer solution obtained from the sponsor. The third model waste used for the castable and pigment studies was a synthetic developer mixture.

The model waste recovered from distilling the used black and white fixer was obtained by distilling 15 gallons of waste to approximately 1 gallon. This 1 gallon was discharged hot and allowed to solidify and dry. The dry residue was found to contain 46.4 weight percent sulfate and 4.3 weight percent sulfite. The remainder is believed to be acetate and water.

The model developer waste was synthesized by combining the chemicals which would be found in a developer solution. This combination is listed in Table 1 in the order in which the chemicals were combined.

TABLE 1. Model Photowaste Developer

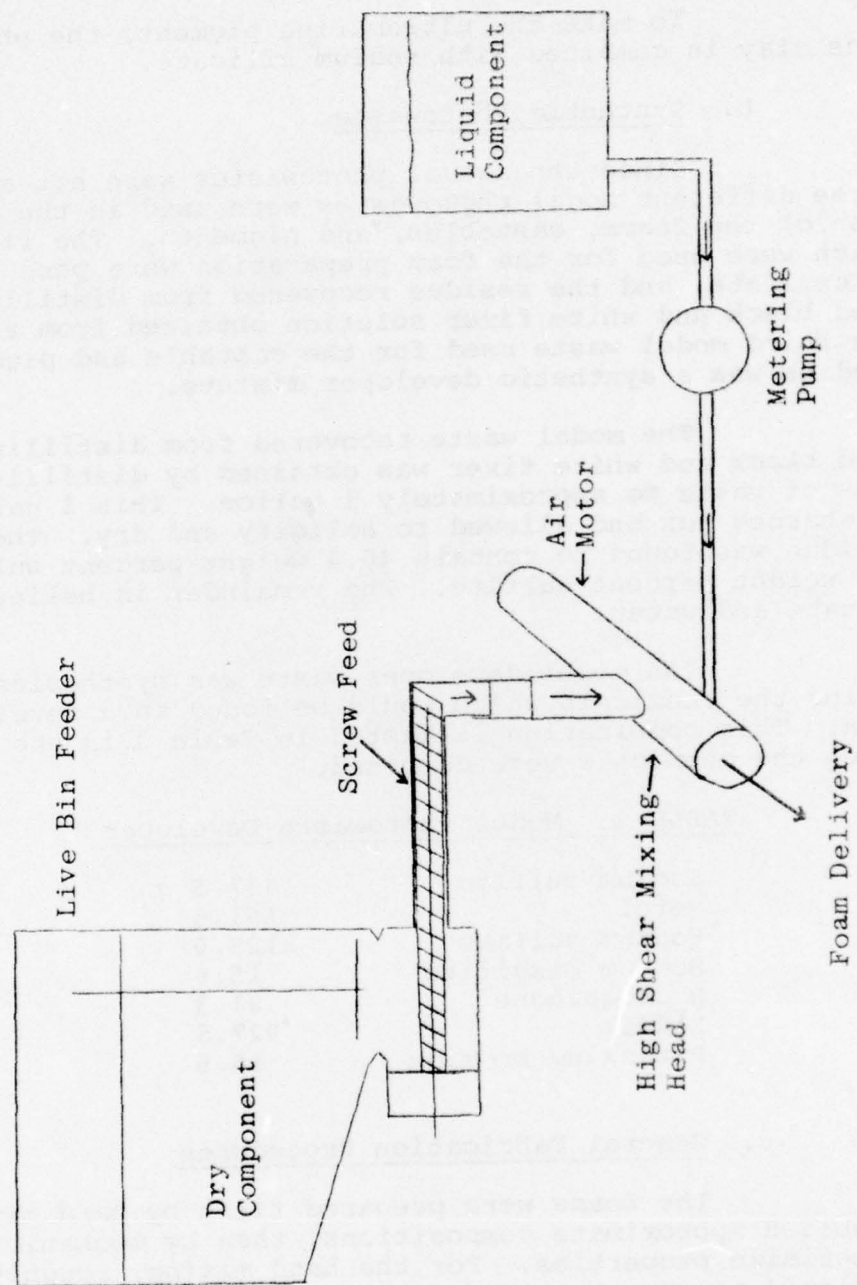
Sodium sulfite	437.5 g
Metol	151.5
Sodium sulfite	1125.0
Sodium bisulfite	15.6
Hydroquinone	81.3
Kodalk	927.5
Potassium bromide	15.6

c. General Fabrication Procedures

The foams were prepared first by hand mixing to establish approximate compositions, then by mechanical mixing to optimize properties. For the hand mixing, roughly 80 grams of liquid component were added with stirring to roughly 100 grams of solid powdered component (containing the micropulverized waste) in a 16 ounce cardboard container. After the approximate foam composition and the solid-to-liquid ratio had been established, the mechanical foaming apparatus shown in Figure 1 was used. This apparatus consists of a gravity fed vibratory bin, capable of holding about 100 pounds of the



FIGURE 1. Foaming Apparatus



solid powdered component, a screw feeder delivering the powder to a high shear mixing head driven by an air motor, a liquid storage reservoir, and a metering pump delivering the liquid to the high shear mixing head. Two different mixing heads were used. They are each composed of a center shaft holding 6 to 9 nests of high shear blades within a cylinder. The liquid and solid components are fed into the cylinder, with the solid component being fed in first. The approximate specifications of the two mechanical mixing heads are as follows:

	<u>Length (in)</u>	<u>O. D. (in)</u>	<u>Maximum Feed Rate (g/min)</u>	<u>(lbs/hr)</u>
Larger head	22	4	1300	172
Smaller head	16	2-1/2	200	26

The castables were hand mixed in quantities up to 5 pounds, by again adding liquid component to solid component.

The ultramarine pigments were prepared on a laboratory scale of batches less than one pound.

2. Amended Contract (February 2, 1975 - February 2, 1976)

a. Disposal and Product Objectives

The objective was the successful incorporation of the photowaste into a ceramic foam or ceramic castable for either sale into the building or refractories markets or for class 3 landfill disposal. Success was to be judged by the wastes being rendered harmless to humans, the ecology and the environment in an economically feasible manner consistent with accepted processing technology. Thus, the scope of the work included testing the waste containing ceramic for commercial properties and pollution hazards; conducting a market study for determining the ceramics most promising applications; and completion of first approximation of the products manufacturing costs.

b. Photowaste

Two different batches of real photowaste were obtained and analyzed. Table 2 gives the analysis of the first photographic waste batch which was a mixture of developer and

fixer. Note that sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) was the primary constituent with small amounts of sulfite ( $\text{SO}_3^-$ ) and sulfate ( $\text{SO}_4^-$ ) and no free sulfur (S), bisulfite ( $\text{HSO}_3^-$ ), or pyrosulfate ( $\text{S}_2\text{O}_5^-$ ). Table 3 gives the analysis of the second waste batch, which was primarily fixer.

TABLE 2. Analysis of First Photowaste Batch

<u>Component</u>	<u>Weight % Measured</u>	<u>Calculated Weight % Sulfur</u>
$\text{S}_2\text{O}_3^-$	35.91	20.54
$\text{SO}_3^-$	4.92	1.97
$\text{SO}_4^-$	0.34	0.11
$\text{HSO}_3^-$	not detected	-
$\text{S}_2\text{O}_5^-$	not detected	-
Total S	22.61	22.62 (sum of above)
Na	16.26	
C	2.07	
$\text{NH}_4$	< 0.01	
Total Halogen as $\text{Cl}^-$	0.15	
K, B	0.05 - 0.5	
Ag, Mg, Si, Fe, Ca, Ni, Al, Cu, Cr	< 0.01	
Sb, Ta, As, Mn, Hf, Pb, W, Ge, Bi, Be, In, Mo, Sn, V, Cd, Ti, Zr, Zn, Co, Sr, Li, Ba	not detected	

The semiquantitative spectrographic analysis indicates the second batch has more impurities than the first. The second batch has a higher percentage of sodium (Na), aluminum (Al), silicon (Si), silver (Ag), lead (Pb), and lithium (Li) than did the first. Quantitative analysis for the second batch shows a lower percentage of thiosulfate ( $\text{S}_2\text{O}_3^-$ ), a higher percentage of sulfite ( $\text{SO}_3^-$ ) and about the same amount of total sulfur as did the first batch.



TABLE 3. Analysis of Second Photowaste Batch

Semi-Quantitative Analysis

<u>Range of Concentration</u>	<u>Elements</u>
> 10%	Na
0.1 - 1%	Al
0.05 - 0.5%	B, K
0.01 - 0.1%	Si, Ag
< 0.01%	Pb, Fe, Li, Cu, Cr, Ca, Mg
not detected	Sb, As, Mn, W, Ge, In, Ni, Bi, Nb, Be, Mo, Sn, V, Cd, Zn, Ti, Zr, Co, Sr, Ba

Quantitative Analysis

<u>Substance</u>	<u>Percentage</u>
Thiosulfate, $S_2O_3^{=}$	15.83
Sulfite, $SO_3^{=}$	10.13
Total sulfur	23.0
$Na_2CO_3$	1.44

Table 4 shows a comparison of the sulfur for the first and second batches. The amount of total sulfur measures (22.61%) for the first batch agrees well with the sum of the calculated weight percentages of sulfur (22.62%) from each component. However, for the second batch, the amount of sulfur measured (23.0%) is greater than the sum of the calculated weight percentages of sulfur (13.10%) from each component. The analyst felt this missing sulfur was in the form of free sulfur.

TABLE 4. Comparison of Sulfur for First  
and Second Photowaste Batch

<u>Component</u>	<u>Wt. % Measured</u>	<u>Wt. % Sulfur</u>	<u>Wt. % Measured</u>	<u>Wt. % Sulfur</u>
Thiosulfate, $S_2O_3$	35.91	20.54	15.83	9.05
Sulfite, $SO_3^-$	4.92	1.97	10.13	4.05
Sulfate, $SO_4^-$	0.32	0.11	not analyzed	-
Total sulfur	22.61	22.62 (sum of above)	23.0	13.10

c. General Fabrication Procedures

The general fabrication procedures for the foams and castables were the same as described in Section III.2.c.

SECTION IV

DATA AND RESULTS

The data and results obtained for the original and for the amended contract will be discussed separately.

1. Original Contract Data and Results

The ceramic foams, ceramic castables, and the ultra-marine pigments will each be discussed in turn.

a. Ceramic Foams

Two different synthetic photowastes were used for the production of the foams since the real photowaste was unavailable at the time. These two synthetic wastes were sodium thiosulfate,  $Na_2S_2O_3$ , or the residue recovered from the distillation of spent black and white fixer solutions. In either case, the micropulverized synthetic waste was incorporated by dry

blending into the solid powdered component. The composition of the solid component is given in Table 5a.

TABLE 5a. Composition of Solids Component

Wollastonite C-1	$\text{CaSiO}_3$	60.8%
Hydral 710	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	3.3
Magnesium oxide, light	$\text{MgO}$	2.2
Photowaste (fixed solids/or $\text{Na}_2\text{S}_2\text{O}_3$ )		33.7
		<u>100.0%</u>

The liquid component was prepared by slowly adding hydrated alumina C-31 to an approximately 90°C solution of phosphoric acid and water. The composition of the liquid component is given in Table 5b.

TABLE 5b. Composition of Liquid Component

(75% N.F.) Phosphoric acid	76.5%
Hydrated alumina C-31 Alcoa $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	13.7
Water	9.8
	<u>100.0%</u>

The solid and liquid components were fed to the mixing head at variable rates permitting modification of the formulation of the foam. Changes in the solid-to-liquid ratio at given overall feed rates influence the properties of the end products, primarily density, cold crushing strength, and thermal conductivity.

Table 6 summarizes the foaming runs which used both the residue from the distilled black and white fixer solution and pure sodium thiosulfate as the synthetic photowastes.

The data in Table 6 were displayed graphically (Figures 2 to 8) to learn if any regular relationship exists between the variables. These graphs show that for sodium thiosulfate as the photowaste, the compressive strength of the foam seems to follow the feed rate (Figure 2), the solid/liquid ratio (Figure 3), and the percent photowaste (Figure 4) in a regular manner. Figure 2 shows that below a total feed rate of 1250 g/min. the compressive strength appears to remain constant. Between feed rates of 1250-1650 g/min. the compressive strength increases



with increased feed rate, and reaches a second constant value for speed rates above 1650 g/min. Similar patterns are evident for the relationship between compressive strength and solid/liquid ratio, and compressive strength and percent photowaste. Figure 3 shows that below a solid/liquid ratio of 1.3, the compressive strength appears constant. Between solid/liquid ratios of 1.3-2.0, the compressive strength increases with an increase in the ratio. Above a ratio of 2.0, the compressive strength remains constant. Figure 4 shows that below a percent photowaste of 19%, the compressive strength appears constant. Between photowaste percentages of 19-22.5%, the compressive strength increases with photowaste content. Above 22.5% the compressive strength remains constant.

TABLE 6. Influence of Feed Rate and Solid/Liquid Ratio on Foam Properties

Sample No.	Solid g/min	Liquid g/min	S/L Ratio	% Photo- waste	Foam Density pcf	Pore Size Range mm	Compressive Strength psi
Sodium Thiosulfate							
2182-24-2	450	260	1.73	21.3	50.5	-	-
-3	580	540	1.07	17.4	45.6	3.0-4.0	127
-4	710	540	1.31	19.1	38.2	-	105
-5	840	540	1.55	20.5	33.8	3.0-4.0	182
-6	1350	540	2.5	24.0	46.7	0.2-0.5	339
-7	960	540	1.77	21.5	35.1	1.0-2.0	279
-8	1100	540	2.03	22.5	35.9	0.5-1.0	337
-9	1230	540	2.27	23.4	41.0	0.5-1.0	334
-10	1230	540	2.27	23.4	52.5	0.5-2.5	492
Fixer Solution Solids							
2182-32-1	840	540	1.56	20.5	51.7	0.2-0.5	564
-2	840	590	1.42	19.7	51.3	0.2-0.5	218
-3	840	590	1.42	19.7	33.5	0.5-1.0	217
-4	840	590	1.42	19.7	30.3	0.5-1.0	258
-5	770	590	1.30	19.0	29.6	0.5-1.0	190
-6	860	590	1.46	20.0	30.0	0.2-0.5	218
-7	860	590	1.46	20.0	32.2	0.2-0.5	305

FIGURE 2. Compressive Strength and Density vs Total Feed Rate  
Run 2182-24

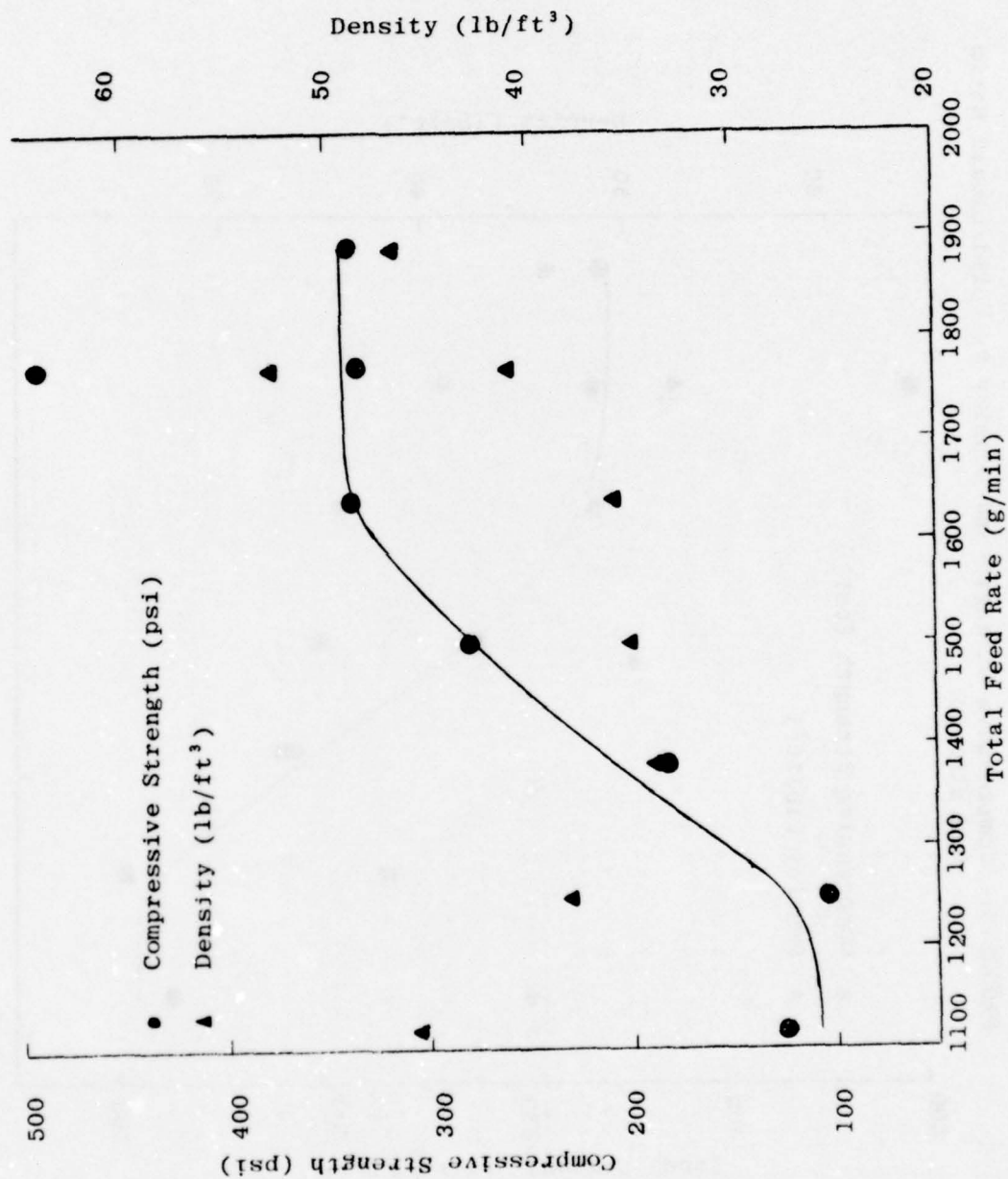


FIGURE 3. Compressive Strength and Density vs Solid/Liquid Ratio  
Run 2182-24

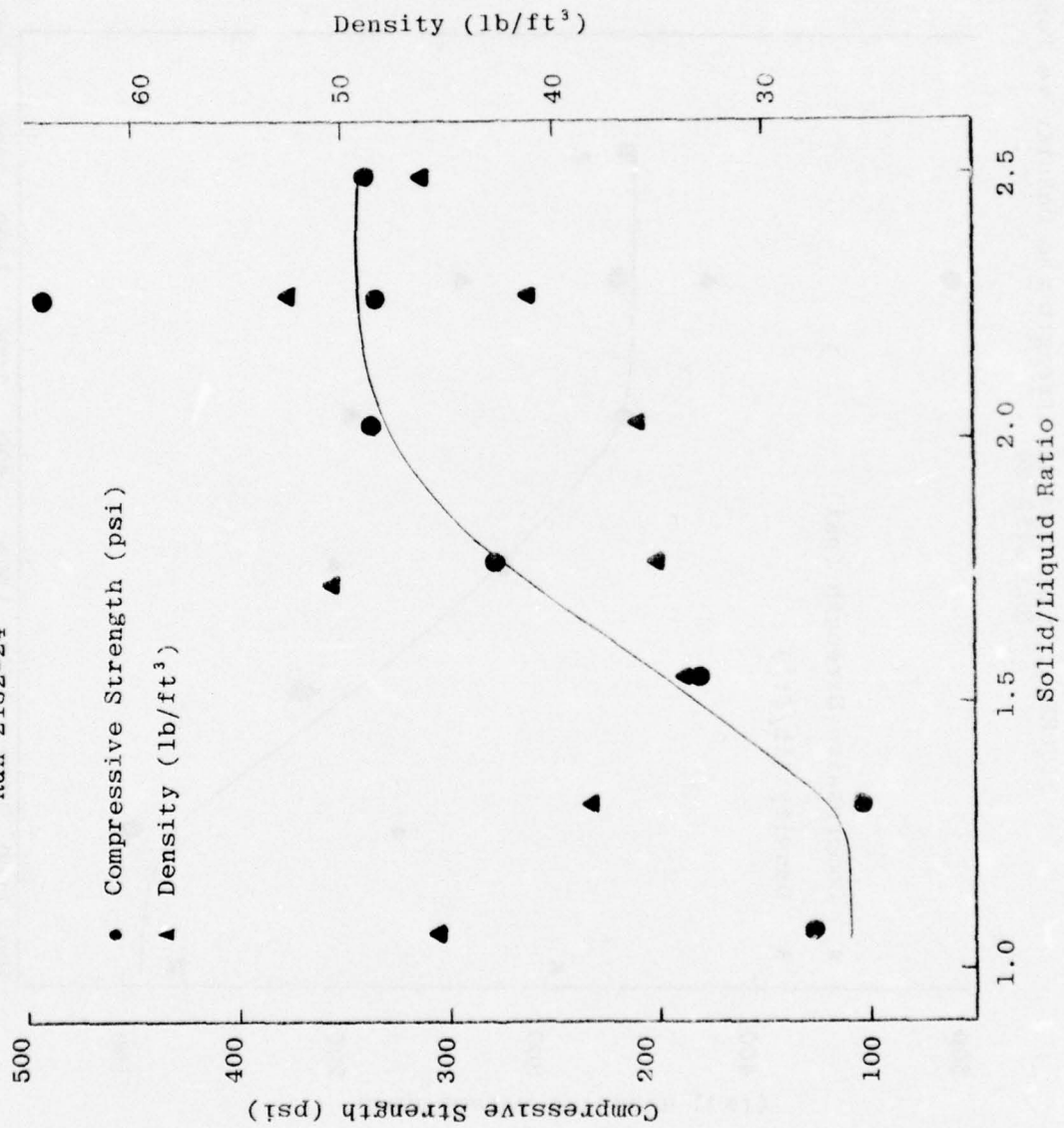
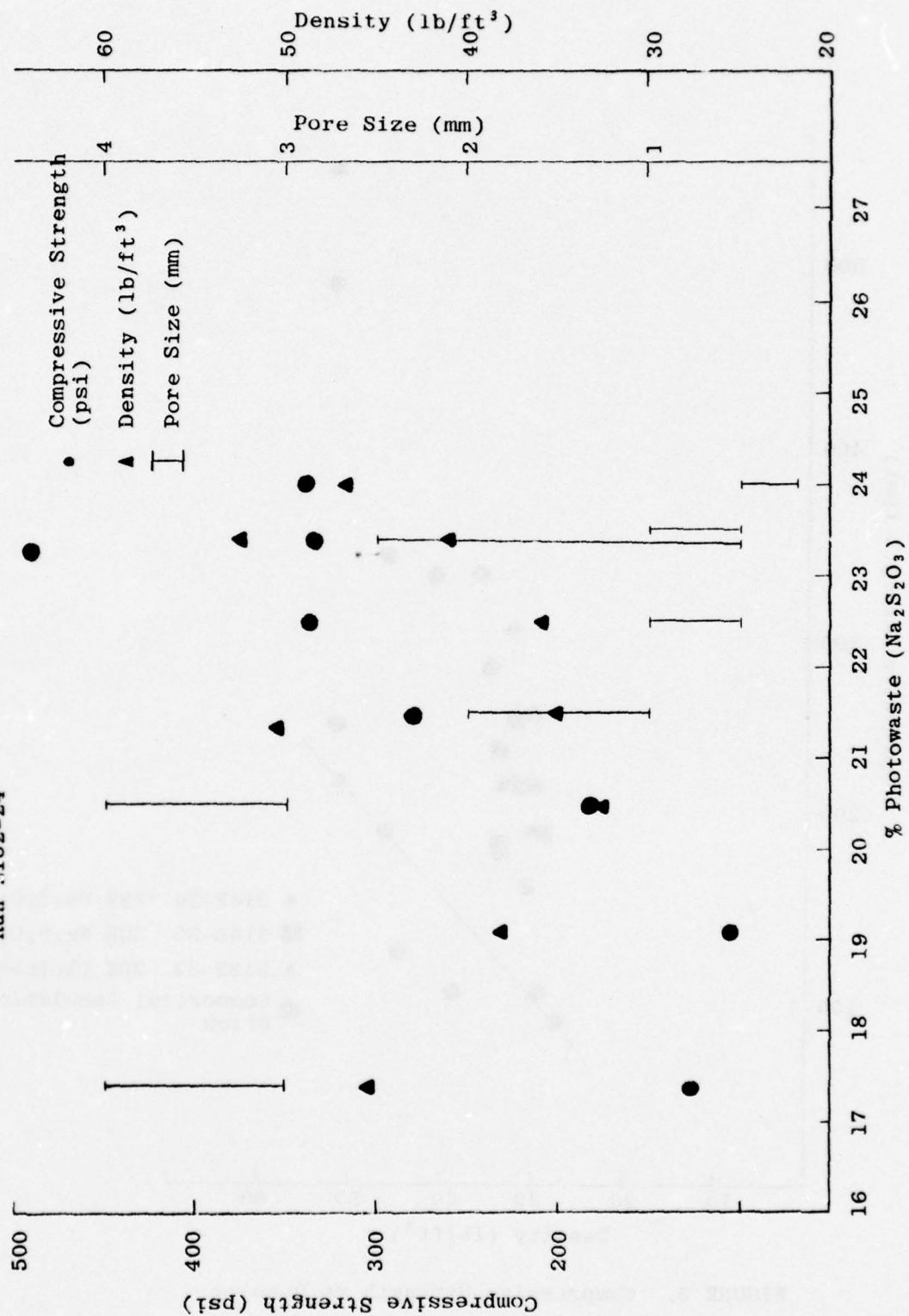




FIGURE 4. Compressive Strength and Density vs % Photowaste  
Run 3182-24



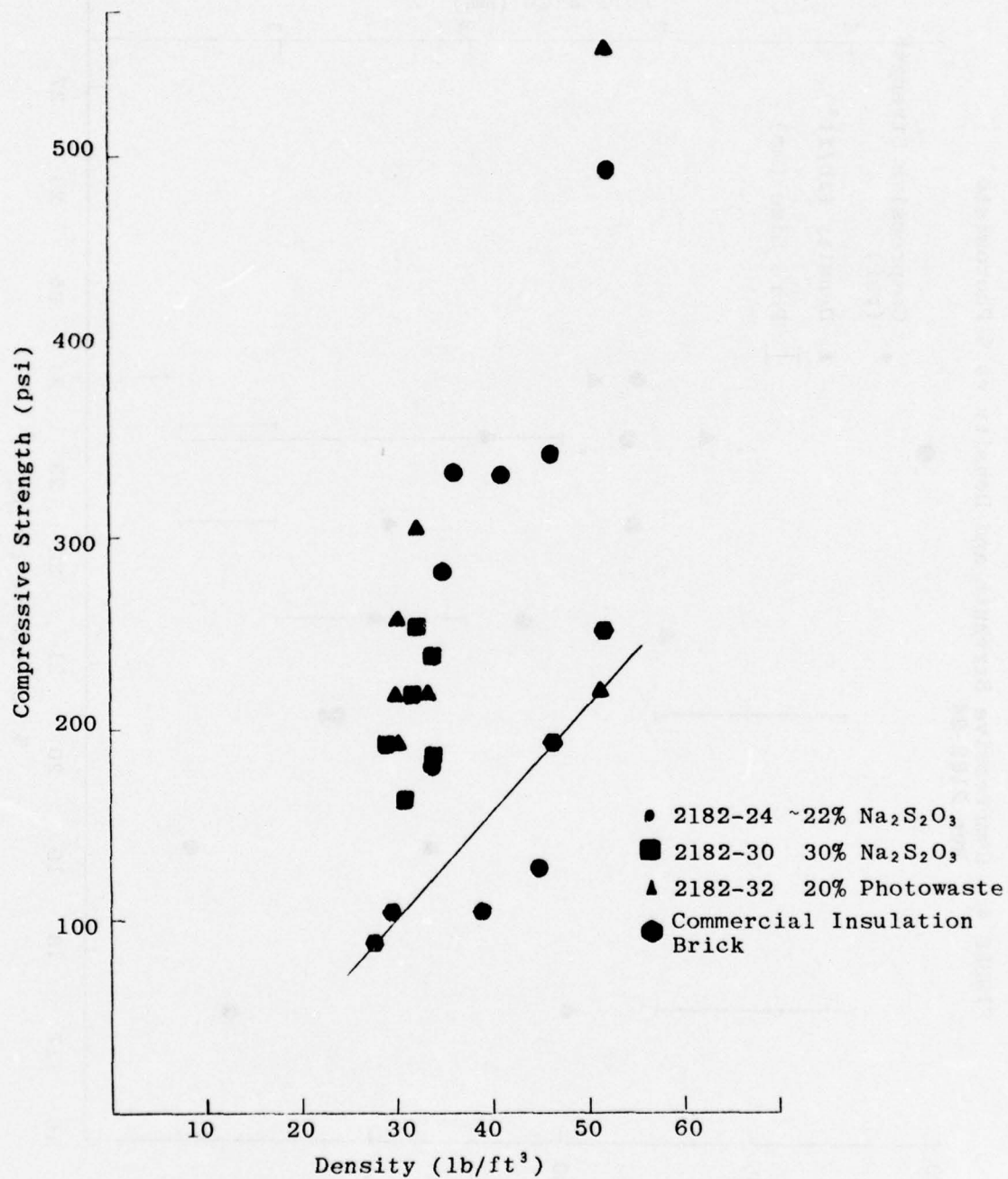


FIGURE 5. Compressive Strength vs Density

FIGURE 6. Compressive Strength and Density vs Solid/Liquid Ratio  
Run 2182-32

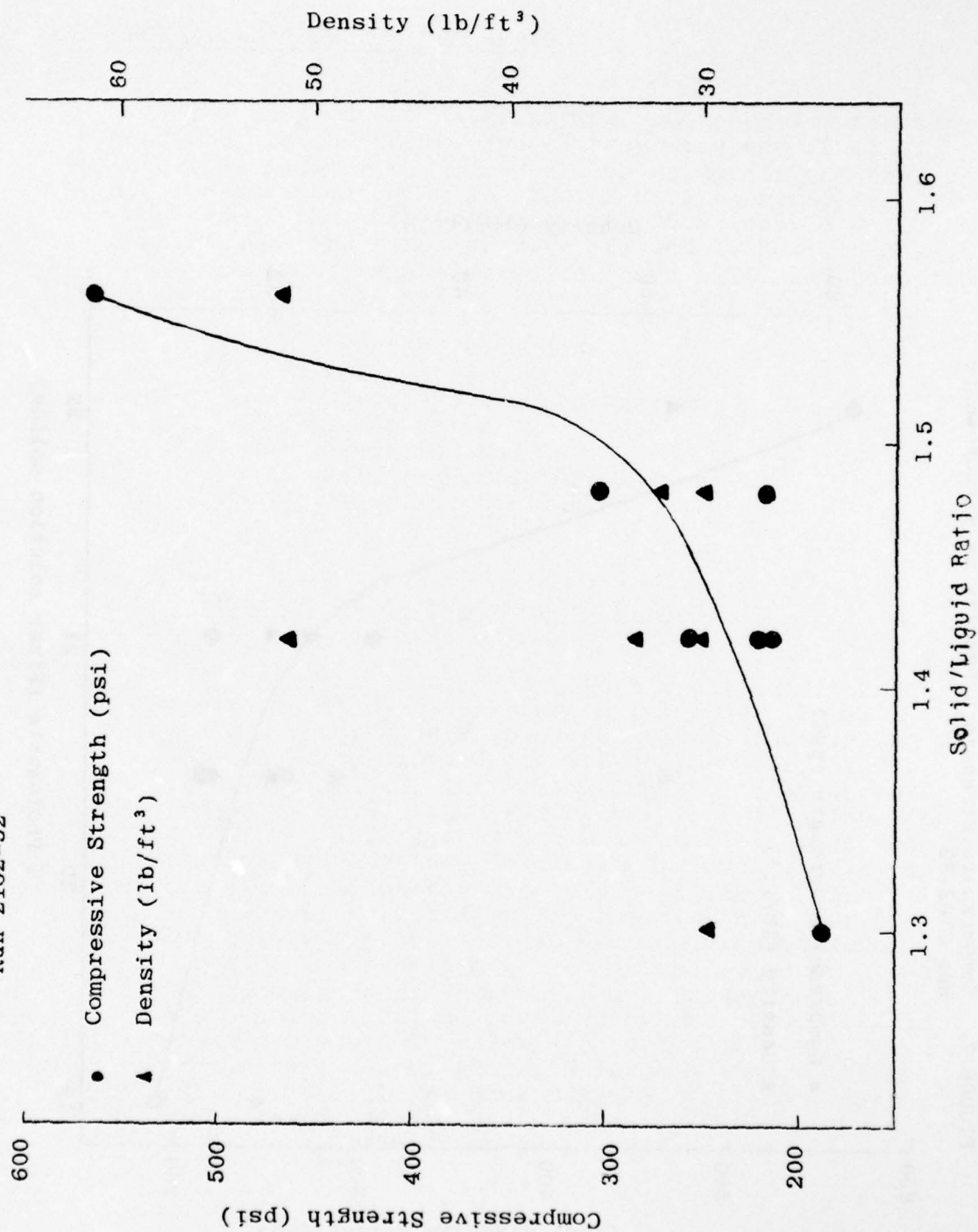




FIGURE 7. Compressive Strength & Density vs % Photowaste  
Run 2182-32

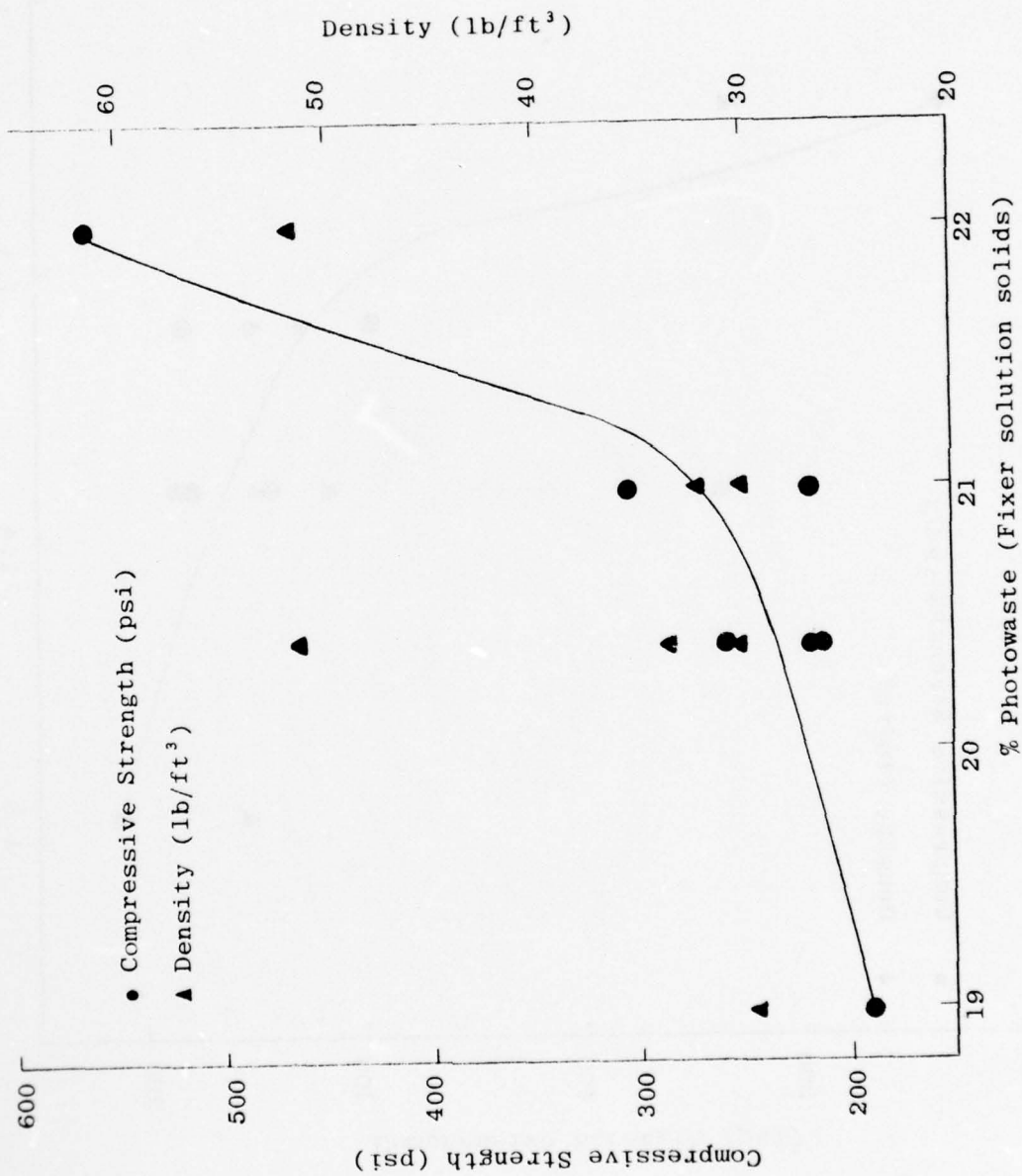
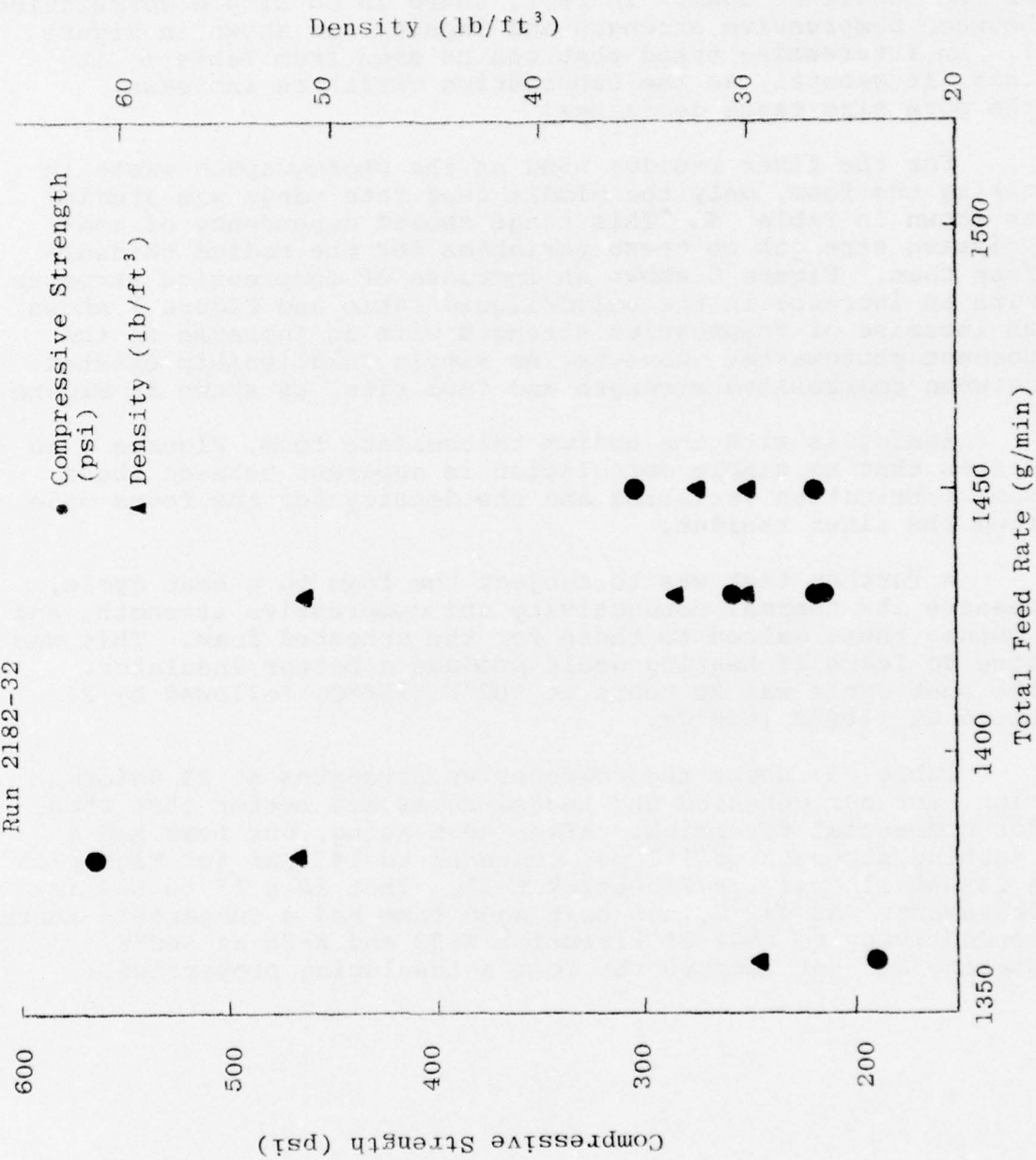


FIGURE 8. Compressive Strength and Density vs. Total Feed Rate  
Run 2182-32



Figures 2 to 4 also show that there is no simple correlation between these same fabrication variables and the density of the resultant foam. In fact, there is no simple correlation between compressive strength and density, as shown in Figure 5. An interesting trend that can be seen from Table 6 is that, in general, as the fabrication variables increase, the pore size range decreases.

For the fixer residue used as the photographic waste in making the foam, only the middle feed rate range was studied, as shown in Table 6. This range showed dependency of compressive strength on these variables for the sodium thiosulfate foam. Figure 5 shows an increase of compressive strength with an increase in the solid/liquid ratio and Figure 7 shows an increase of compressive strength with an increase in the percent photowaste. However, no simple relationship existed between compressive strength and feed rate, as shown in Figure 8.

Again, as with the sodium thiosulfate foam, Figures 6 to 8 show that no simple correlation is apparent between these same fabrication variables and the density for the foams made from the fixer residue.

A further test was to subject the foam to a heat cycle, measure its thermal conductivity and compressive strength, and compare these values to those for the unheated foam. This was done to learn if heating would produce a better insulator. The heat cycle was 20 hours at 302°F (150°C) followed by 24 hours at 1200°F (649°C).

Table 7 shows the compressive strengths at 3% deformation, for our unheated and heated foams are better than those for commercial firebrick. After heat aging, our foam had a crushing strength of 167 psi compared to 145 psi for Firebrick K-23 and 110 psi for Firebrick K-20. That is a 15 to 50% improvement. At 482°F, our heat aged foam had a comparable thermal conductivity to that of Firebrick K-23 and K-20 at 500°F. Heating did not improve the foam's insulating properties.



TABLE 7. Properties of Heat Aged Foams  
Compared to Commercial Firebrick

	2182-32-3	2162-41 aged 20 hrs/302°F (+ 24 hrs/1200°F)	Firebrick K-20	Firebrick K-23
<u>Crushing Strength (psi)</u>				
at failure	323	174	-	-
at 3% deformation	116	167	110	145
<u>Density (pcf)</u>	33	28	29	31
<u>Thermal Conductivity (Btu/hr/°F/ft /in)</u>				
212°F	0.83	0.90	-	-
482°F	1.18	1.25	-	-
500°F	-	-	0.9	1.1
1292°F	-	-	1.5	1.5

b. Castables

As an examination of an alternate product form, a mix of developer chemical was incorporated with a silicate binder solution and a block material was obtained. Such material could find construction applications similar to cement blocks. The material was pressed to remove excess binder and oven dried at 260°F. The oven dried material was further thermally treated to 1800°F with attendant observation of density change and weight loss. The material had good mechanical properties. Table 8 presents the composition of the castable.

TABLE 8. Castable Composition

Model Photowaste Developer (see Table 1)		21.8%
Wollastonite	93.5%	
Hydral 710	5.6%	
MgCO <sub>3</sub>	0.9%	
	<u>100.0%</u>	65.4%
30% Sodium Silicate Solution		12.8%
		<u>100.0%</u>

Table 9 presents the response of the composition to thermal treatment.

TABLE 9. Castable Firing

<u>Firing Temperature</u>	<u>Time (min)</u>	<u>% Weight Loss</u>	<u>Density (pcf)</u>
500°F	30	2.3	94
1000°F	30	4.6	87
1800°F	30	5.1	94 (some shrinkage)

c. Ultramarine Pigments

Ultramarine pigments are derived [Ref. 20, 21, 22, 23, 24, 25] by heating mixtures of sulfur, clay, alkali, and a reducing agent at high temperatures. Ultramarine blues are complex sodium alumino sulfosilicates which find application as artist colors, roofing granules, coloring soap powders, and tinting aids in white paint. They are used where color permanence, brilliance and alkaline resistance are of importance. Ultramarine is also used as a catalyst in the dehydration of isopropyl alcohol, the oxidation of sulfur in petroleum products, and hydrocracking and sulfur removal from thiophenes.

- 
20. G. Yamaguchi and Y. Kubo, Ultramarine Synthesized Under Controlled Vapor Pressures, Bull. Chem. Soc. of Japan, 41 2645 (1968).
  21. R. Van Order and R. H. Hill, Manufacture of Ultramarine Blue, U. S. Patent 2,806,802.
  22. W. J. Kruppa, et al., Manufacture of Ultramarine, U. S. Patent 2,700,618.
  23. E. W. Large, Ultramarine Blue, Am. Perfumes Cosmet. 77 (91 42-44 (1962)).
  24. F. Moser, Ultramarine Pigments, pg. 409, Pigment Handbook Vol. I, ed. T. C. Patton, J. Wiley & Sons, Inc. (1973).
  25. J. T. Morrison, Ultramarine Pigments, Paint and Varnish Prod., 61 pg. 59-64 (August 1971).

is: A typical composition of ultramarine blue [Ref. 26]

SiO <sub>2</sub>	37 to 50%
Al <sub>2</sub> O <sub>3</sub>	23 to 29%
Na <sub>2</sub> O	19 to 23%
S	8 to 14%

The nature of the manufacturing methods of ultramarine blue [Ref. 20, 21, 23, 24, 25] indicates that photowaste derived from developer, and hence containing sulfur compounds and organic residues, would be useful as a source of the sulfur and reducing agent needed to generate the S<sub>2</sub><sup>=</sup>, and S<sub>5</sub><sup>-</sup> color centers in an alumino silicate matrix.

To that end a brief investigation in the preparation of ultramarine blue was attempted. The procedure involved the dry blending of photowaste developer with a clay and some sodium silicate solution.

64.8% Model Photowaste Developer (see Table 1)

27.8% H. H. Pulverized Clay

7.4% Starso Sodium Silicate Solution

The above mixture was placed in fireclay crucibles and fired to 1500°F for 30 minutes. The charge was highly colored in a gradation indicating slight differences of reducing environment. Regrinding and refiring produced a less marked change in coloration. Microscopic examination showed a wide distribution of coloration with some particles intensely colored blue while others showed some brownish red character. On grinding the material dry in a ball mill, a fine powder was produced. Both ultramarine blue and green were obtained, though in an impure state.

An investigation of the literature was initiated to gauge the market and the potential of processes to prepare the ultramarine pigments from photowaste materials.

We determined that all the ultramarine blue was being imported into the country from Europe and Japan. This amounted to about 9 million pounds per year, then at an import value of about \$3,000,000. This may represent a retail value of about \$10,000,000 since the price range was \$0.42 per pound to \$1.75 per pound, depending on grade of material.

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26. Ultramarine Blue, ASTM D262-47.



The quantity of ultramarine pigments which was imported annually is presented in Table 10.

TABLE 10. Ultramarine Pigments Tariff Schedule No. 4738400\*

<u>Year</u>	<u>Net Quantity (lbs)</u>	<u>Dollar Value</u>	<u>Price/Pound</u>
1970	3,568,522	\$ 775,898	\$0.2174
1971	3,844,586	1,003,656	0.2608
1972	6,672,192	2,321,631	0.3408
1973	9,063,195	-	-
1974	3,548,790 (first six months)	-	-

\* [Chemical Marketing Reporter; International Commerce Dept. of U. S. Dept. of Commerce.]

An apparently anomalous increase in import of pigment occurred in 1972; this may be attributed to a number of domestic manufacturers stopping production for probably reasons of antiquated equipment and pollution control problems.

The reasons for discontinued production of ultramarine in this country are tied to the enactment of rigid air pollution controls and the extremely lengthy process for production. Some newer techniques of production involve closed atmosphere ovens and continuous production rotary kilns. The domestic market of about \$10,000,000 did not appear to warrant the investment needed for a several million pound production facility with several different grades and colors of ultramarine blue.

## 2. Amended Contract Data and Results

Most of the research effort was devoted to the ceramic foams, with the castables receiving a minor effort. Each will be discussed in turn.

### a. Ceramic Foams

With arrival of the real photowastes plus interest in using accepted processing techniques, some compositional changes in the foam formulation were needed. These changes were aimed at minimizing sulfur release during foam fabrication,

and eliminating it from the cured product. In order to minimize sulfur release during foam fabrication, the amount of acidity encountered by the thiosulfate is minimized. Thus the photowaste is combined with the dry powder basic oxides component, and the ratio between the powder component and the liquid phosphoric acid component is such as to prevent the final mix from becoming too acidic. The foams were found to be capable of containing up to 12% by weight of photowaste. Also, to prevent the foams from setting up too quickly after the acidic component was combined with the photowaste containing basic oxide component, weakly basic oxides like iron oxide were substituted for part of the strongly basic oxide magnesium oxide in the powder component, and some magnesium oxide was added to the phosphoric acid liquid component.

Table 11 gives specific successful formulations for the foams. These foams cured at room temperature were odorless, had densities of 16 to 23 pcf, and cold crushing strengths of 36 to 102 psi. These same foams fired to 1000°F had negligible density changes, and cold crushing strengths of 65 to 200 psi.

TABLE 11. Foam Formulations

<u>Dry Component</u>		<u>Dry Component</u>	
Material	Wt. %	Material	Wt. %
Wollastonite	48.8	Wollastonite	43.0
Hydral 710	4.0	Hydral 710	3.5
MgCO <sub>3</sub>	4.0	MgCO <sub>3</sub>	3.5
Photowaste	34.1	Photowaste	30.0
Red Fe <sub>2</sub> O <sub>3</sub>	9.1	Fe <sub>2</sub> O <sub>3</sub> (red)	10.0
	<u>100.0</u>	Carbon black	
		(Sterling N.S.)	10.0
			<u>100.0</u>
<u>Liquid Component</u>			
Material	Wt. %		
75% H <sub>3</sub> PO <sub>4</sub>	58.3		
C-31 Alumina	10.5		
MgO	3.2		
Water	28.0		
	<u>100.0</u>		

TABLE 11 (continued)

The approximate ratio of dry component to liquid was 1.6:1. Thus, for the non-carbon black containing foam, the overall composition was:

Component	Wt. %
Wollastonite	30.0
Hydral 710	2.5
Magnesium carbonate	2.5
Iron oxide	5.6
Photowaste	21.0
75% Phosphoric acid	22.4
Alumina C-31	4.0
Magnesium oxide	1.2
Water	10.8
	<u>100.0</u>

If the mixing machinery and application can tolerate a very rapid set-up time, then the formulations given in Table 12 are acceptable.

TABLE 12. Rapid Setting Foam Formulations

<u>Component</u>			
Photowaste	10.8	5.4	10.8
Wollastonite C-1	27.2	44.6	39.6
Alumina 710	1.6	2.6	2.3
Alumina C-31	4.8	4.8	4.8
Magnesium carbonate	0.6	1.0	0.9
Magnesium oxide	1.8	1.9	1.9
Clay	13.5	-	-
75% phosphoric acid	26.8	26.8	26.8
Water	12.9	12.9	12.9

The densities of the odorless foams given in Table 12 range from 27 to 36 pcf with cold crushing strengths of 200-325 psi.

#### b. Ceramic Castables

For combining the primarily sodium thiosulfate into the castable, the photowaste was combined with the powder component. The castable was capable of incorporating up to 22% by



weight of photowaste. Table 13 gives typical castable formulations. These castables cured at room temperature, were odorless, had densities of 77 to 104 pcf, and cold crushing strengths of 450 to 2600 psi. These same castables cured at 1000°F were odorless, had densities of 75 to 93 pcf, and cold crushing strengths of 300 to 2300 psi.

TABLE 13. Castable Formulations

<u>Dry Component</u>		<u>Liquid Component</u>	
Material	Wt. %	Material	Wt. %
Wollastonite C01	25.0	N-38 Sodium silicate	100.0
MgO	30.0		
Clay (Kaolin)	25.0		
Photowaste	20.0		
	<u>100.0</u>		<u>100.0</u>

Dry/Liquid - 1/1

<u>Dry Component</u>		<u>Liquid Component</u>	
Material	Wt. %	Material	Wt. %
Wollastonite C01	25.0	N-38 Sodium silicate	50.0
MgO	30.0	Water	50.0
Clay (Kaolin)	25.0		
Photowaste	20.0		
	<u>100.0</u>		<u>100.0</u>

Dry/Liquid = 1/1

<u>Dry Component</u>		<u>Liquid Component</u>	
Material	Wt. %	Material	Wt. %
Wollastonite C-1	25.0	N-38 Sodium silicate	50.0
Alumina 710	25.0	Water	50.0
MgO	30.0		
Photowaste	20.0		
	<u>100.0</u>		<u>100.0</u>

Dry/Liquid = 1/1

### c. Environmental Exposure of Foams and Castables

Several different foam and castable compositions incorporating the photowastes were given 20 days exposure to three different leaching solutions: hard tap water, 10% sodium hydroxide (pH = 14), and 0.01% (pH = 2) hydrochloric acid. Tables 14, 15, and 16 summarize the results. Table 14 reports the ceramic foams, Table 15 the ceramic castables, and Table 16 the semiquantitative analysis of the leach solutions for selected foam and castable samples. Only those samples which survived leaching solution exposure virtually unchanged were tested for crushing strength, and of these only some of the better ones had their final leaching solutions tested for sulfur, metals and alkali metals content.

The following observations were made:

- Foams:
- (1) Those receiving water and acid exposure survived better than those receiving alkaline exposure.
  - (2) For the room temperature cured foams, those not containing clay were stronger.
  - (3) For the 1000°F cured foams, those containing clay were stronger.
  - (4) The majority of the foams did not emit an odor in any of the solutions; and only a very slight initial sulfur odor was emitted from the others.
  - (5) For the room temperature cured foams, the order of sulfur leaching was base>water>acid. The maximum sulfur concentration in the leach solution was 4200 ppm or 0.42%.
  - (6) The foams cured at 1000°F had at most 550 ppm or 0.055% sulfur leaching.
  - (7) The semiquantitative analysis showed that sodium, calcium, and magnesium were leached out to levels not exceeding 5000 ppm; potassium, silicon, and boron to levels between 5 and 50 ppm; and aluminum, copper, nickel, and lead to levels between 0.5 and 5 ppm. The only metal of any concern is the lead, which was probably contained in the clay which was used in some of the samples. The suggested safe maximum lead ingestion per day for adults is 0.6 mg. If the leach solution contains the maximum of 5 ppm, then an adult could safely ingest 120 ml or about 4 ounces of the leach solution per day.

TABLE 14. Exposure Tests for Ceramic Foams

	Room Temperature Cure			1000°F Cure		
	2429-27-1	2429-27-2	2429-27-3	2429-27-1	2429-27-2	2429-27-3
Uncured Formulation (%):						
Photowaste	10.8	5.4	10.8	10.8	5.4	10.8
Wollastonite C-1	27.2	44.6	39.6	27.2	44.6	39.6
Alumina 710	1.6	2.6	2.3	1.6	2.6	2.3
Alumina C-31	4.8	4.8	4.8	4.8	4.8	4.8
Magnesium carbonate	0.6	1.0	0.9	0.6	1.0	0.9
Magnesium oxide	1.8	1.9	1.9	1.8	1.9	1.9
Clay	13.5	-	-	13.5	-	-
75% Phosphoric acid	26.8	26.8	26.8	26.8	26.8	26.8
Water	12.9	12.9	12.9	12.9	12.9	12.9
Est. P. W. % when Cured	12	6.9	11.7	12.5	7.3	14.6
Exposed 20 days in	Initially very slight odor and small pH			No odor. No pH change.		
Hard Tap Water	change from			No appearance change.		
	5 to 7	5 to 6.5	5 to 7	No odor. No pH change.	No odor or pH change.	No odor or pH change.
10% Sodium hydroxide	Sample generally soft and surrounded by crystals.			Slight change in appearance with powder on bottom of beaker.		
0.1% Hydrochloric acid	No odor or pH change.			No odor or pH change.		
	No appearance change.			No appearance change.		
Thermal Conductivity						
BTU-in./ft <sup>2</sup> .hr.°F @ 212°F	0.90			Very slight appearance change.		
@ 500°F	1.04					



TABLE 14. (continued)

	Room Temperature Cure			1000°F Cure		
	2429-27-1	2429-27-2	2429-27-3	2429-27-1	2429-27-2	2429-27-3
Density (pcf)	35.8	27	32.7	34.5	24.7	32.5
Crushing Strength (psi):						
Unexposed controls	210	204	328	176	44	214
(2 samples each)	103	164	296	153	109	136
Water exposed	181	338	298	334	65	126
10% NaOH exposed	-	41	68	269	41	76
0.01% HCl exposed	136	236	146	150	111	168
Sulfur in Leach						
Solution (mg/l or ppm)						
Water exposed	1525	-	2544	327	514	-
10% NaOH exposed	-	-	4209	-	-	-
0.01% HCl exposed	-	-	1860	-	550	-

TABLE 15. Exposure Tests for Ceramic Castables

Uncured Formulation (%):	Room Temperature Cure				1000°F Cure			
	2429-15	2429-15-1	2429-17	2429-21	2429-15	2429-15-1	2429-17	2429-21
Photowaste	10.0	10.0	10.0	20.0	10.0	10.0	10.0	20.0
Wollastonite C-1	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
MgO	15.0	15.0	15.0	7.5	15.0	15.0	15.0	7.5
Clay	12.5	12.5	-	10.0	12.5	-	-	10.0
N-38 Sodium silicate	50.0	25.0	25.0	50.0	50.0	25.0	25.0	50.0
Water	-	25.0	25.0	-	-	25.0	25.0	-
Alumina 710	-	-	12.5	-	-	-	12.5	-
Est. P. W. % when Cured	11	13	12	22	13.2	15.6	14.1	26.4
Exposed 20 Days in Hard Tap Water	Fell apart into large pieces.	Very slight change. Some powder ppt. out.	Fell apart into large pieces.	Totally disintegrated.	Unchanged.	Unchanged.	Unchanged.	Very slight change. Some powder ppt. out.
10% Sodium hydroxide	No odor	No odor	No odor	No odor	SO <sub>2</sub> odor.	SO <sub>2</sub> odor.	No odor	SO <sub>2</sub> odor.
	Fell apart into large pieces.	Totally Disintegrated			Unchanged.	Unchanged.	Fell apart into large pieces.	Very slight change. Some powder ppt. out.
0.01% Hydrochloric acid	No odor	No odor	No odor	No odor	No odor	No odor	No odor	No odor
	Very Slight Change Some powder ppt. out.			Totally disintegrated.	Very slight change. Some powder ppt. out.	Unchanged.	Unchanged.	Very slight change. Some powder ppt. out.
	No odor	No odor	No odor	No odor	SO <sub>2</sub> odor	No odor	No odor	SO <sub>2</sub> odor

TABLE 15. (continued)

	Room Temperature Cure				1000°F Cure			
	2429-15	2429-15-1	2429-17	2429-21	2429-15	2429-15-1	2429-17	2429-21
Density (pcf)	104	77	77	93	93	75	81	84
Crushing Strength (psi):								
Unexposed controls	2600	613	438	2026	2300	723	311	1700
Water exposed	-	313	-	-	>1000	-	-	-
10% NaOH exposed	-	-	321	-	>1000	1050	-	715
0.1% HCl exposed	-	-	-	-	1800	961	-	740
Sulfur in Leach								
Solution (mg/l or ppm):								
Water exposed	-	-	-	-	8559	-	-	-
10% NaOH exposed	-	-	-	-	9919	-	-	-
0.01% HCl exposed	-	-	-	-	9122	-	-	-



TABLE 16. Contents of Selected Leach Solutions

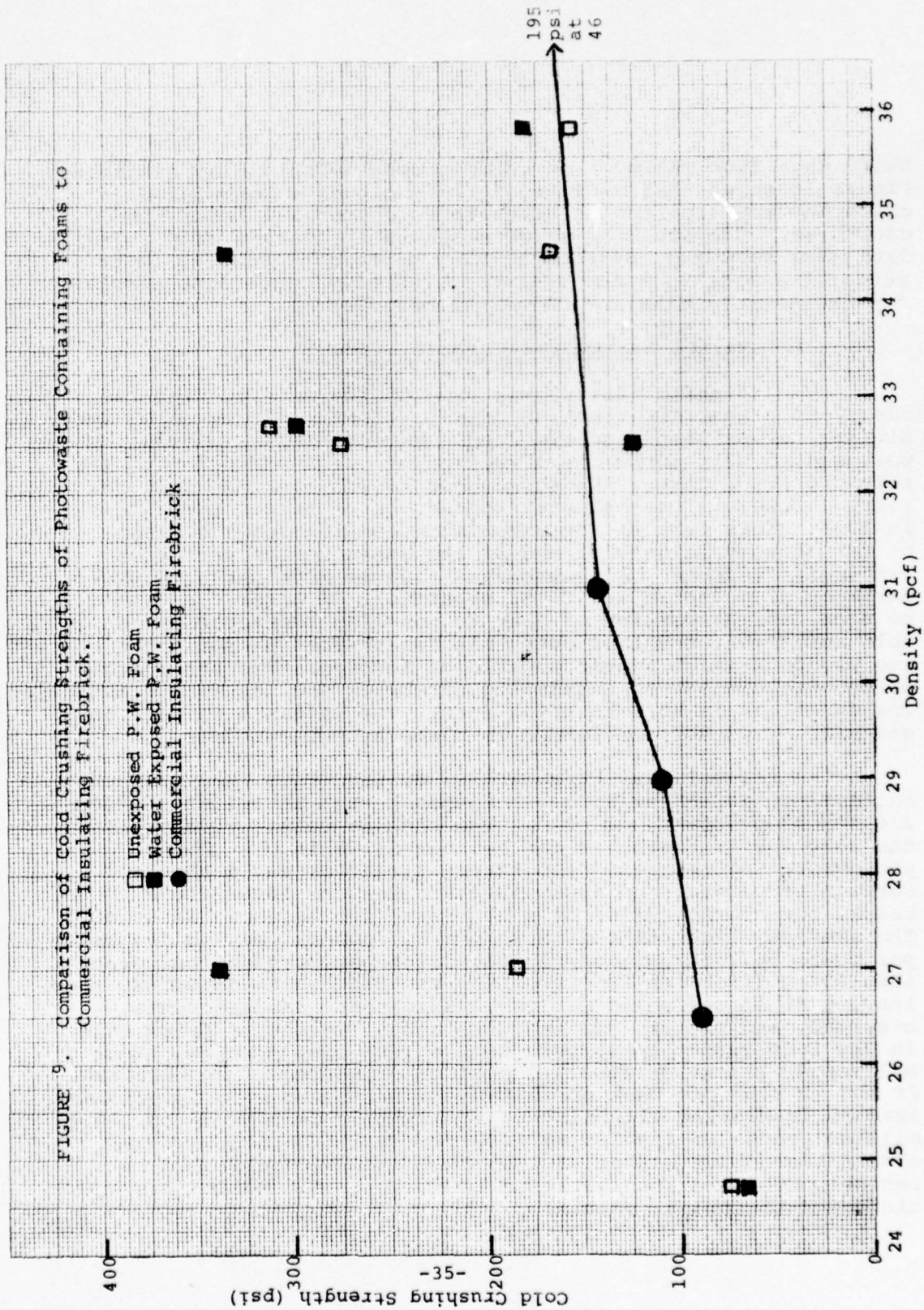
Concentration (ppm)	Hard Water Control	Foam Sample 2429-27				Castable Sample 2429-15			
		-3 (12% P.W.) R.T. Cure		-1 (12% P.W.) R.T. Cure		13% Photowaste		100°C Cure	
		Water Exposure	Clay	Water Exposure	Clay	Water Exposure	0.1% Exposure	10% NaOH Exposure	
50,000-		-	-	-	-	-	-	-	Na
250,000									
5,000-		-	-	-	-	Na	Na	Si	
50,000									
500-		Na	Na	-	-	-	-	Al	
500		Ca	Mg, Ca	Mg, Ca		-	-	K, B	
10-		Mg	Si	Na		K, Mg	K, Mg	-	
100	Na								
5-		K, B, Si	K, B	B, Si		Ni, Ca, B, Si	B, Si	Fa, Mg, Ca	
50							Ca	Ni, Mo	
1-	Si	-	-	-	-	Fe			
10									
0.5-	K, Ca	Al, Cu	Ni, Al, Cu, Pb	Al		Al		V, Ag	
5.0	Fe, Al, Cu, Mg	Li, Fe, Ag	Li, Fe, Ag	Ag, Li, K, Fe, Cu		Ag, Li, Cu	Li, Al, Cu, Fe	Cu, Cr	
1.0		Ba, Sb, Mn, Pb, As, W, Ge, In, Ni, Bi, Sb, Be, Mo, Sn, V, Cd, Zr, Zr, Co, Ti, Cr, Sr	Ba, Sb, Mn, As, W, Ge, In, Bi, Sb, Be, Mo, Sn, V, Cd, Zn, Zr, Co, Ti, Cr, Sr	Ba, Sb, Mn, Pb, As, W, Ge, In, Bi, Sb, Be, Mo, Sn, V, Cd, Zn, Zr, Co, Ti, Cr, Sr		Ba, Sb, Mn, Pb, As, W, Ge, In, Bi, Sb, Be, Mo, Sn, V, Cd, Zn, Zr, Co, Ti, Cr, Sr	Ba, Sb, As, Mn, Pb, W, Ge, Cr, Sb, Bi, Co, Ni, In, Be, Mo, Sn, V, Ti, Zr, Cd, Ag, Zn, Sr	Li, Ba, Sb, Mn, As, Pb, W, Ge, In, Bi, Ti, Sb, Be, Sn, Cd, Zr, Zn, Co, Sr	
not detected	B, As, Mn, Pb, Cr, Co, Ge, Ni, Sr, Bi, Co, Be, Ti, Mo, Zr, Sn, V, Cd, Ag, W, In, Zn, Sb								

Using data from Table 14 for the photowaste-containing foams, Figure 9 shows that the photowaste-containing foams, either unexposed or water exposed, are stronger or about the same as commercial insulating firebrick. The data also show that the 1000°F cured (preferable) or the room temperature cured foams would be suitable for Class 3 landfill photowaste disposal if the landfill is not excessively alkaline.

Castables:

- (1) The 1000°F cured castables were superior in strength to the room temperature cured castables.
- (2) For both the room temperature and 1000°F cured samples, the ones exposed to the acid leach solution survived the best.
- (3) None of the room temperature cured samples emitted a sulfur odor in any of the leach solutions.
- (4) Of the 1000°F cured samples, the ones exposed to base leach solutions did not give off a sulfur odor, but those exposed to water solution did.
- (5) Of the 1000°F cured samples which did not give off a sulfur odor, those samples exposed to a base leach put 9919 ppm of sulfur into the solution while those exposed to an acid leach put 9122 ppm sulfur into the solution.
- (6) More sulfur was leached from the castables than from the foams.
- (7) The castables put more sodium into the leach water than did the foams. The sodium level was between 5000 and 50,000 ppm.
- (8) Species like potassium, magnesium, silicon, aluminum, calcium, and boron were present in slightly larger concentrations for the castable leach solutions than for the foam leach solutions. The only species which may be of some concern is chromium, but it was present at a concentration of < 1 ppm.

FIGURE 9. Comparison of Cold Crushing Strengths of Photowaste Containing Foams to Commercial Insulating Firebrick.





Using data from Table 15 on the photowaste-containing castables, Figure 10 shows that certain of the photowaste-containing castables are superior in strength to commercial insulating castables. The superior samples generally contain clay. The data also show the 100°F cured clay containing samples to be better than the room temperature cured clay containing samples for excessively alkaline Class 3 landfills.

#### d. Market Survey for Ceramic Product

A market survey was made of the refractories industry with special attention paid to those products which were similar to our waste incorporated ceramics. This information was used to help shape the direction of our R & D effort. The refractories industry has shown good growth over the last few years. However, the industry appears to be headed for a loss in 1975. This fact is not surprising considering the slump of the economy in general and of the construction sector in particular. Table 17 summarizes figures from the U. S. Department of Commerce and U. S. Department of Labor. As can be seen, the proportion of clay to non-clay refractories has held relatively constant over this recent time period. The two products which appear capable of incorporating the photowastes are similar to insulating firebrick and insulating castables. The firebrick is sold in brick form. The castable is sold as a granular or powder and formed in-place by the customer.

Insulating firebrick is divided into four broad categories, dependent upon use temperature: 1600-2000°F, 2000-2300°F, 2300-2800°F, >2800°F. The highest volume category is the 2300-2800°F brick, as can be seen in Table 18. The photowaste incorporating insulating firebrick would have a service temperature to about 2000°F. For the 1600-2000°F brick, the average price of a 9" brick, fob Augusta, is \$0.40. The average weight of this brick is 1.7 pounds, making its price per pound \$0.235. The approximate cost per pound of our green insulating firebrick incorporating the photowaste is \$0.08, thus leaving \$0.15 per pound for processing cost, capital costs, overhead, and profit. If half the annual volume of brick sold in the 1600-2300°F group were in the 1600-2000°F range, about 7 million 9" bricks or about 12 million pounds would be required. If the 10 tons per week of photowaste available were incorporated into an insulating firebrick at a weight percentage of 10, 10.4 million pounds of insulating firebrick could be made. Thus, almost the entire market of 1600-2000°F brick would have to become photowaste incorporating in order to accommodate the anticipated photowaste volume.

FIGURE 10. Comparison of Cold Crushing Strengths of Photowaste Containing Castable to Commercial Insulating Castables.

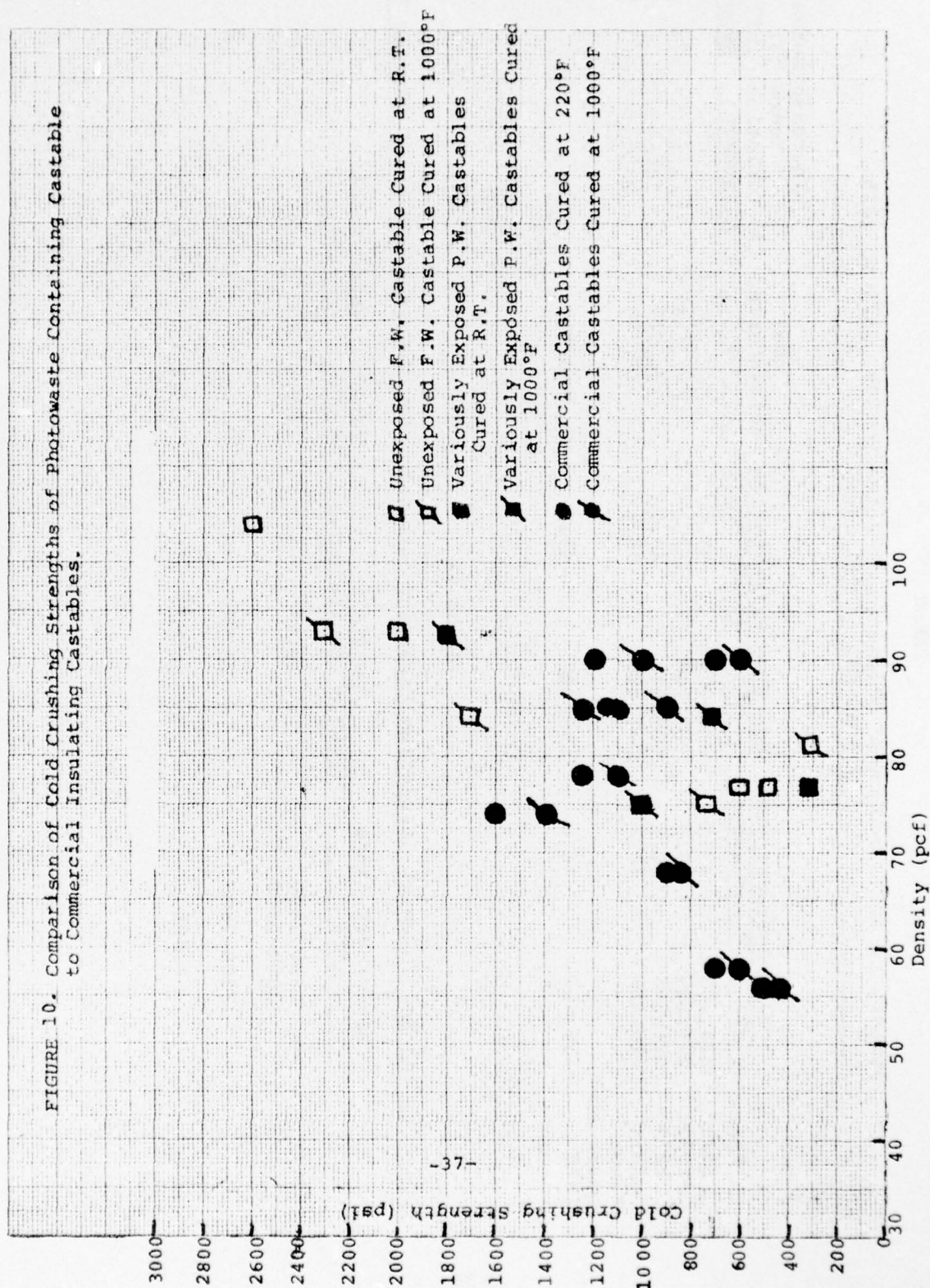


TABLE 17

Summary of U.S. Producers' Shipments of Refractories, 1971 to 1975  
(thousands of dollars)

Year	Clay Refractories (\$)	(% of total)	Non Clay Refractories (\$)	(% of total)	Total Refractories (\$)	No Inflation Adjustment	Increase Between Years (%)	Inflation Adjustment
1971	238,783	42.4	324,838	57.6	563,621			
1972	274,007	43.0	363,148	57.0	637,155	13.1	10.2	
1973	327,265	41.9	453,034	48.1	780,299	22.5	15.0	
1974	410,153	41.9	567,619	58.1	977,772	25.3	14.3	
First 3 quarters 1975	310,455	44.4	387,707	55.6	699,162	-4.7	-11.7	

TABLE 18

## Quantity and Net Value of Insulating Firebrick Shipments for U.S. through Third Quarter 1975

Temperature Range (°F)	Quantity (1000 9" equivalents)	Value (\$1000)	Value/Brick (\$)
1600-2000	10,671	3,829	0.359
2000-2300			
2300-2800	25,988	11,576	0.445
>2800	6,639	4,911	0.740



Insulating castables had a net value of shipments for U.S. productions through the third quarter of 1975 of \$8,424,000 for 36,064 S ton or \$0.12 per pound. The cost per pound for insulating castables most similar to ours is about \$0.18, fob Georgia, Missouri and Pennsylvania. The approximate cost per pound of our insulating castable is about \$0.095, thus leaving \$0.09 per pound for processing and capital costs (which are minimal for castables), overhead and profit. The annual production of insulating castables is about 96 million pounds. Assuming, again, a 10% by weight photowaste incorporation, the anticipated 10 tons per week of photowaste would require about one-ninth of the insulating castables market.

e. Capital Equipment

Table 19 lists the capital equipment needed for processing ten tons per week of photowaste into insulating firebrick. If all of the photowaste is processed into insulating castables, then items 12 through 24 are not necessary. Figures 11, 12 and 13 show the conceptualized work flow for making insulating firebrick, insulating firebrick raw materials to be sold as such, and insulating castables.

Table 20 lists the equipment needed for making a portable unit for producing 20 pounds per minute of cold setting foam incorporating the photowaste. Figure 14 is a conceptualized diagram of the portable unit capable of operation in climates in temperatures from -30° to 120°F. Such a unit would enable the use of available on-site fillers.

The equipment costs and layout are only to be considered a first rough approximation.

f. Direct and Indirect Charges

As stated earlier, the materials cost per pound is \$0.08 for the brick and \$0.095 for the castable. Assuming the plant converts half of its photowaste into brick and half into castable, the yearly materials cost would be \$910,000 for a 10.4 million pound output. If the plant produces all brick, the materials cost is \$832,000; if the plant produces all castables, the materials cost is \$988,000.

If the plant runs three 8-hour shifts a day, about 8 to 10 men per shift will be needed depending upon product distribution as shown in Table 21.

TABLE 19

Capital Equipment for Facility

1.	Solid Storage Bins	\$ 5,000	
2.	Dry Blender	8,500	
3.	Grinder	2,500	
4.	Pulverizer	5,300	
5.	Vibratory Hopper	2,500	
6.	Air Conveyors	40,000	
7.	Materials Handling Equipment	15,000	
8.	Air Compressors	15,000	
9.	Bagging Equipment	14,000	
10.	Weighing Scales	1,000	
11.	Q. C. Lab	<u>40,000</u>	\$148,800
12.	Liquid Storage S.S. Tanks	\$ 1,500	
13.	Metering Pumps	11,000	
14.	Foam Heads	5,000	
15.	Molds	5,000	
16.	Conveyor Belt	10,000	
17.	Drying Oven	50,000	
18.	Firing Kiln	200,000	
19.	Pumps (air operated)	2,000	
20.	High Speed Mixers	600	
21.	Valves 2" S.S.	2,000	
22.	Valves 2" S. S. (air operated)	4,400	
23.	Pipe 2" S.S.	10,000	
24.	Temperature Controls	<u>1,800</u>	\$303,300
			<u>\$452,100</u>

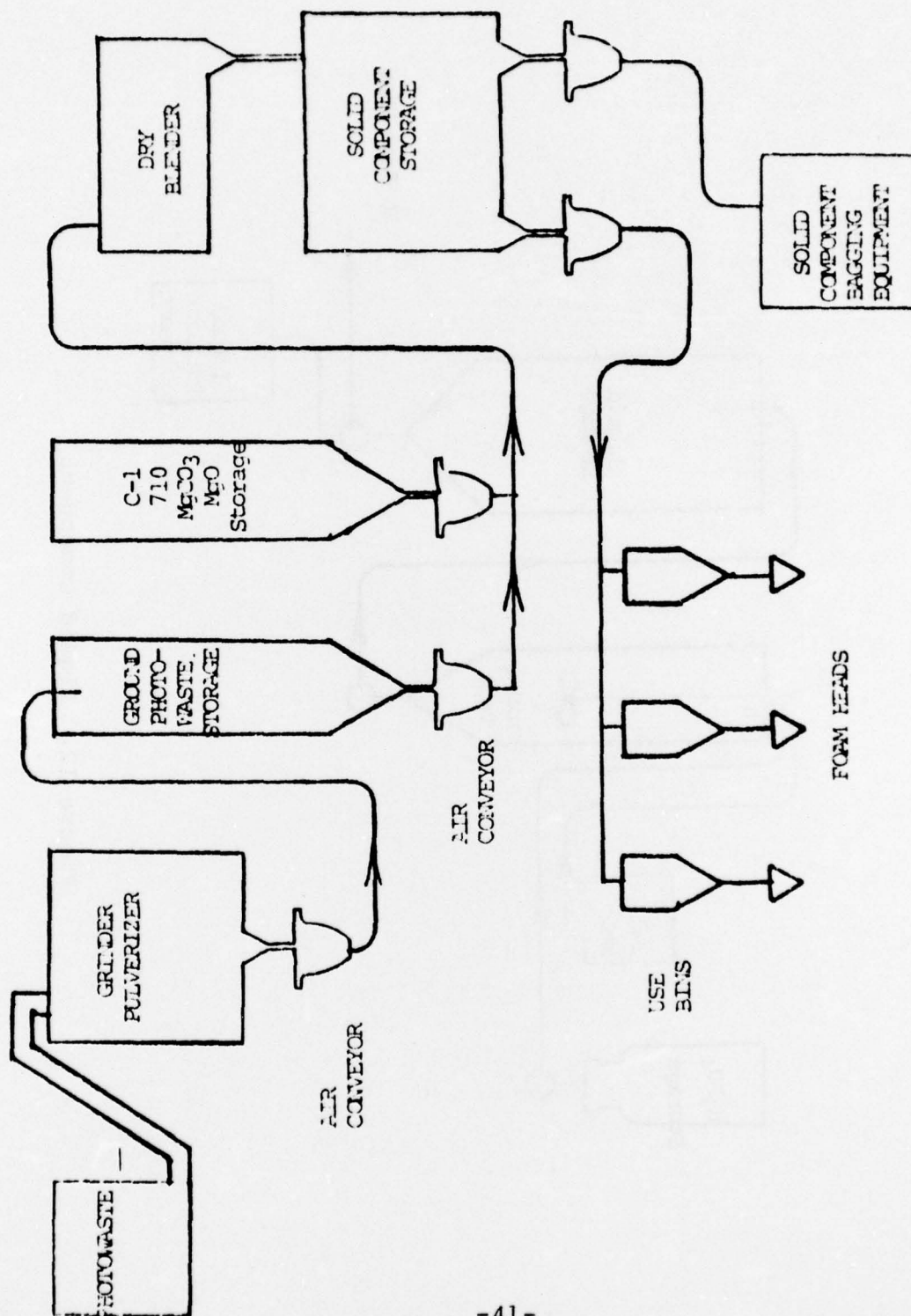


Figure 11. Dry Component



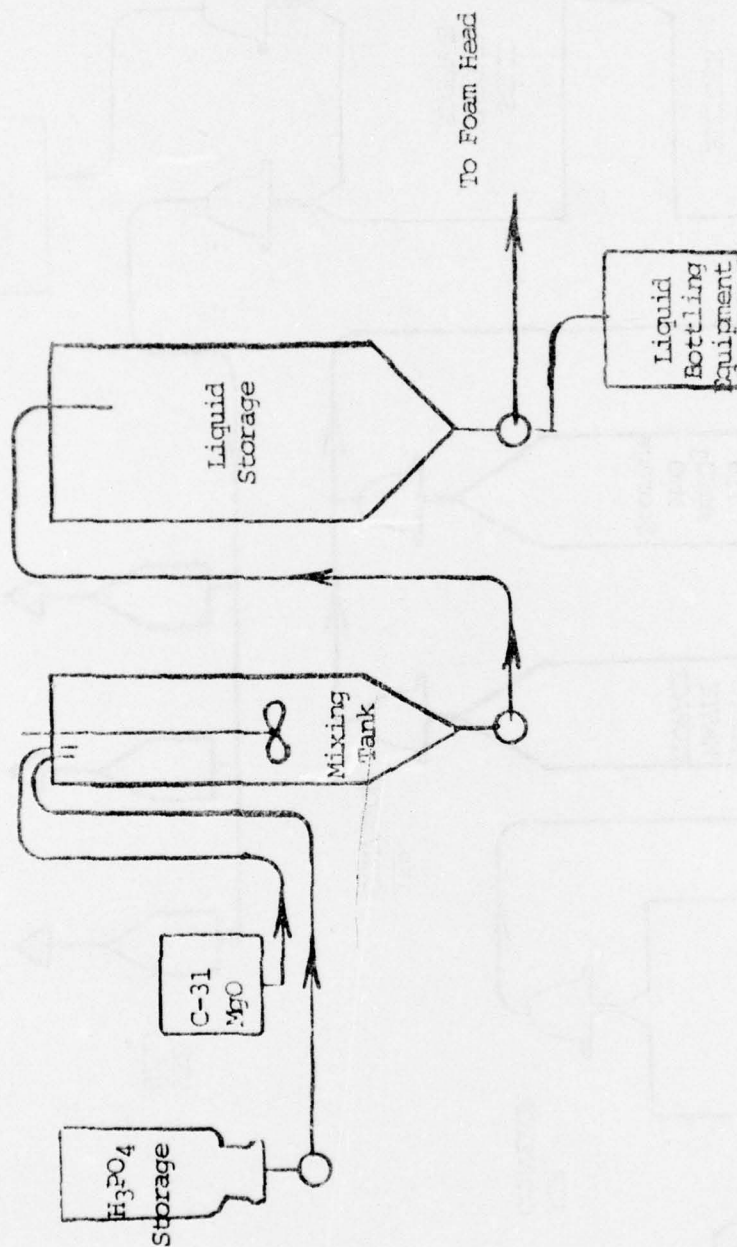


Figure 12. Liquid Component

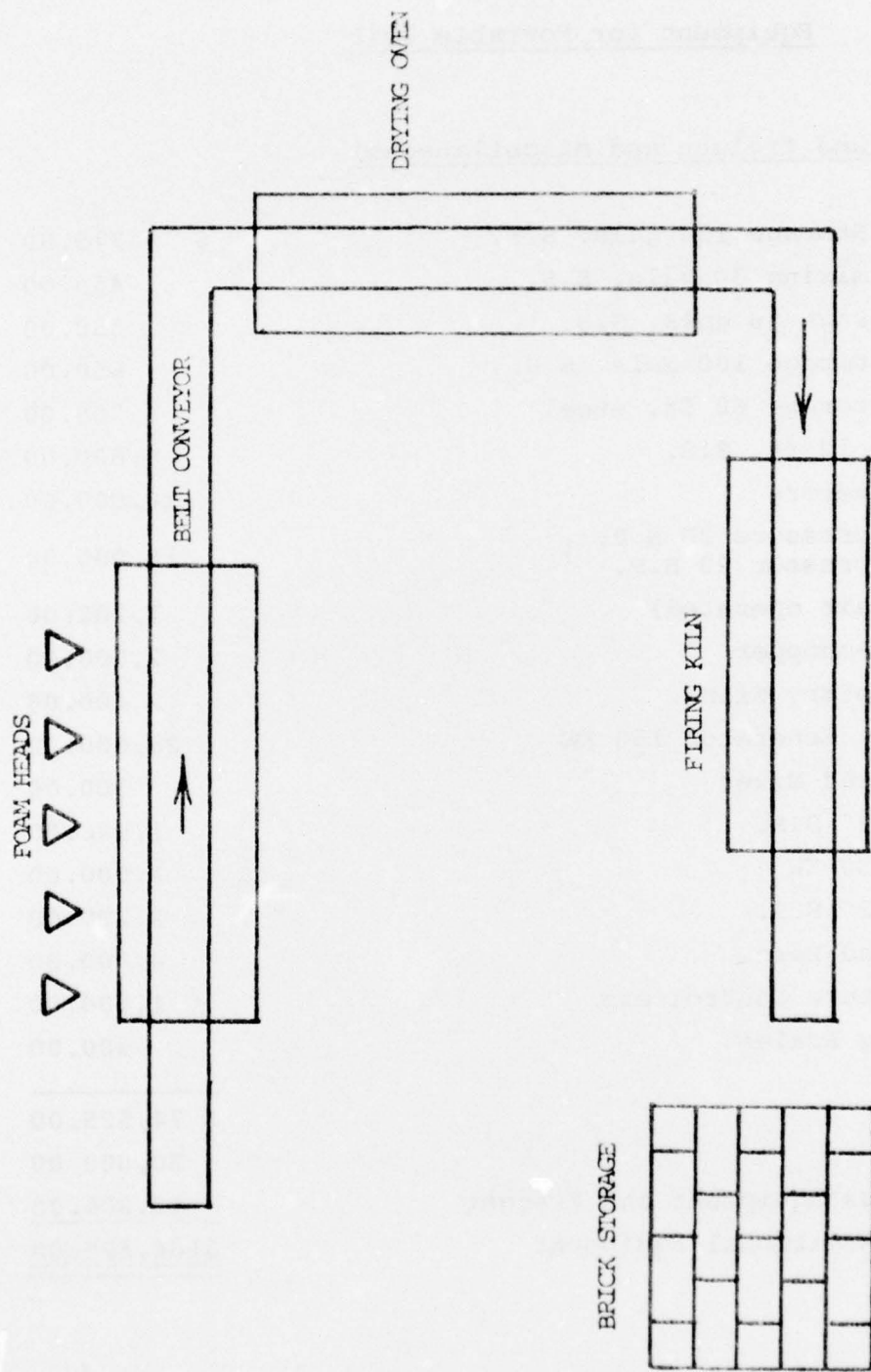


Figure 13. Foam Fabrication

TABLE 20

Equipment for Portable UnitEquipment (and freight and miscellaneous)

1	Liquid Storage 150 gals. S.S.	\$ 775.00
1	Liquid Mixing 30 gals. S.S.	450.00
1	H <sub>2</sub> O Storage 50 gals. S.S.	550.00
1	H <sub>3</sub> PO <sub>4</sub> Storage 100 gals. S.S.	650.00
1	Solid Storage 60 ft. steel	500.00
1	Blender 12 ft. S.S.	6,600.00
2	Air Conveyors	10,000.00
2	Air Compressors 20 H.P. }	15,000.00
1	Air Compressor 20 H.P.	
4	Pumps (air operated)	1,200.00
1	Grinder-chopper	2,000.00
1	Dryer Rotary Kiln	400.00
1	Electric Generator 150 KW	25,000.00
1	High Speed Mixer	300.00
4	Valves 2" S.S.	1,000.00
1	Heater 50 KW	2,500.00
11	Valves 2" S.S.	2,200.00
	Pipes and Hoses	4,000.00
	Temperature Controllers	1,000.00
	Weighing Scales	400.00
		<hr/>
		\$ 74,525.00
	Pilot Model	20,000.00
	Miscellaneous Equipment and Freight	<hr/> 10,000.00
	Total Additional Equipment	<hr/> <hr/> \$104,525.00



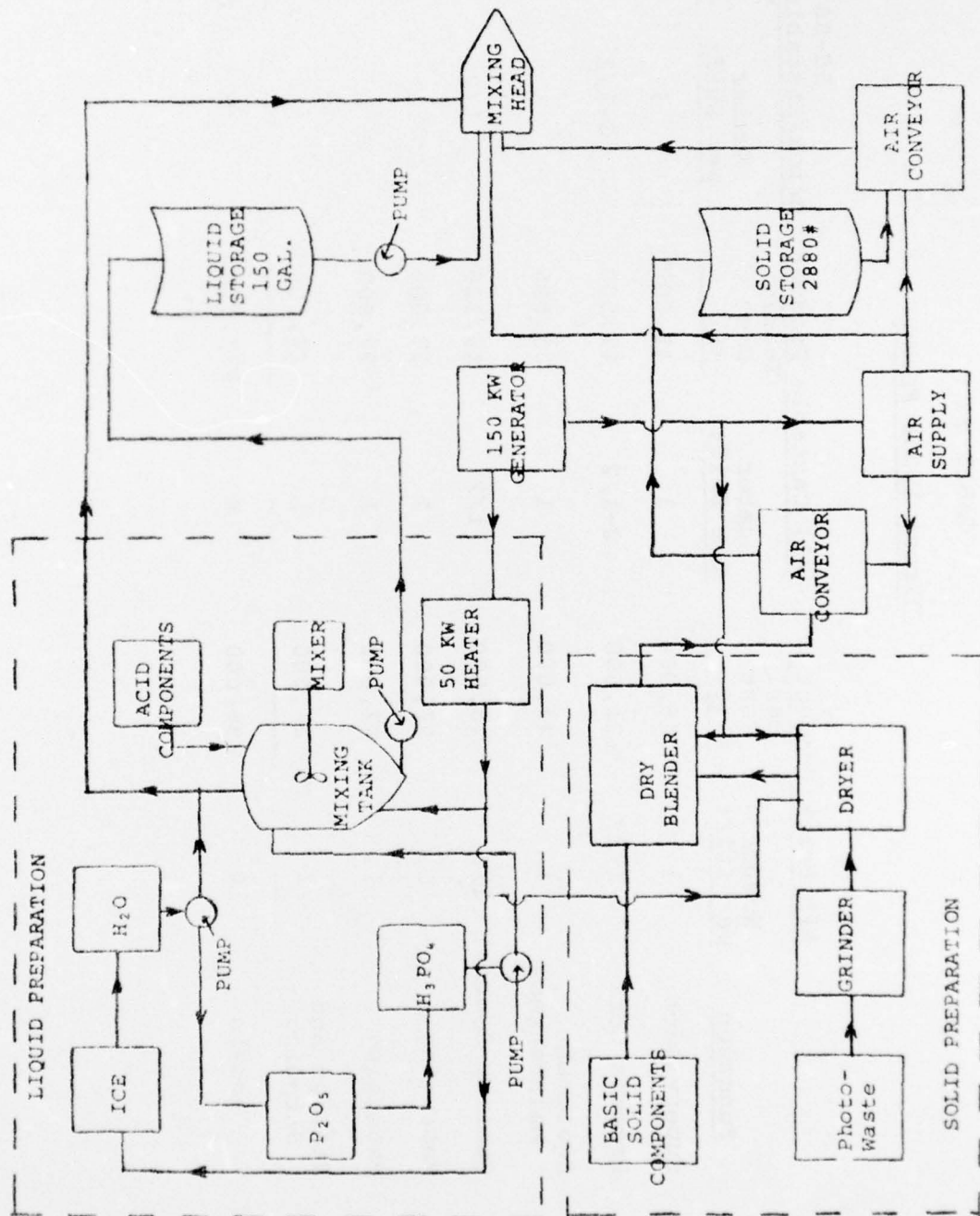


Figure 14. Conceptual Equipment Design for Portable Unit

TABLE 21

Direct Labor Force

Function	All Brick Product		All Castable Product		Brick/Castable Product		50-50
	Number per Shift	Yearly Cost (\$)	Number per Shift	Yearly Cost (\$)	Number per Shift	Yearly Cost (\$)	
Supervision	1	45,000	1	42,000	1	44,000	
Process Work	4-1/2	121,500	2-1/2	67,500	3-1/2	94,500	
Equipment Maintenance	1	33,000	1	33,000	1	33,000	
Quality Control	1/2	13,500	1/2	13,500	1/2	13,500	
Receiving	1	27,000	1	27,000	1	27,000	
Packaging	1	27,000	1	27,000	1	27,000	
Storage and Shipping	1	27,000	1	27,000	1	27,000	
Totals	10	294,000	8	237,000	9	266,000	

Power requirements are difficult to estimate without a finalization of equipment and plant design. Consequently, an arbitrary figure of \$100,000/year will be used.

Indirect charges include such items as capital equipment depreciation, occupancy, secretarial, accounting, building and property maintenance, shipping and postage, insurances, executive salaries, advertising, etc., and are estimated at 100% of direct.

g. Production Costs

For a plant producing 0.4 million pounds per year of insulating firebrick and insulating castables, the estimated costs are given in Table 22.

TABLE 22

<u>Production Costs</u>			
	<u>All Brick</u>	<u>All Castables</u>	<u>50/50 Brick/Castables</u>
Labor	\$ 294,000	\$ 237,000	\$ 266,000
Materials	832,000	988,000	910,000
Power (Arbitrary)	100,000	100,000	100,000
Direct Charges			
Total	\$1,226,000	\$1,325,000	\$1,276,000
Indirect (100%)	1,226,000	1,325,000	1,276,000
Total Costs	\$2,452,000	\$2,650,000	\$2,552,000
Cost/lb.	\$0.236	\$0.255	\$0.245
Commercial Cost/lb	\$0.235	\$0.18	

Note the arbitrary power costs due to not having a refined plant layout and equipment specifications. Assuming the numbers used are valid, it appears possible for the insulating firebrick to be made at a profit after a little belt tightening, but not the castables.



TABLE 23

Comparison of Properties for our Ceramic  
Foam and Castable to Commercial Products

	Our Foam	Insulating Firebrick		Our Castable	Insulating Castable B & W Kaolite		
		B&W K1620	B&W K-20		2200	2200 LI	2200 HS
Service Temperature (°F)	to 2000	1600	2000	2200	2200	2200	2200
Density (pcf)	27 - 35	27	29	75 - 100	58	56	74
Cold Crushing Strength (psi)	200 - 300	90	110	600 - 2600	700	500	1600
Thermal Con- ductivity							
BTU·in/ft ·hr (°F)	0.9	-	-	-	1.6	1.6	1.9
212°F	1.0	0.9	1.0	-			
500°F							

## SECTION V

### DISCUSSION AND CONCLUSIONS

The objective for the amended contract was to economically dispose of the waste material either by its incorporation into a useful product or by its being rendered harmless and suitable for a class 3 landfill. To this end two odorless products have been identified as well as a means of safe disposal.

These two products are a ceramic foam capable of being used as an insulating firebrick and a ceramic castable, capable of being used as an insulating castable. Each green product contains about 10% by weight of the photowaste. Table 23 compares the properties of our ceramic foam and castable with commercial products by Babcock & Wilcox. For the properties we tested, our products were about identical or somewhat better, particularly the cold crushing strength. As shown in Section 4.2, apparently the photowaste incorporating foam might be sold at profit as an insulating firebrick, but not the castable, unless our rough cost figures are overly high. The manufacturing costs for the foam are estimated at 23.6 cents per pound, and for the castable at 25.5 cents per pound. Comparable commercial products sell at 23.5 and 18 cents per pound, respectively. Obviously, some belt tightening is needed for the foam to turn a profit.

From the environmental exposure tests, for safe photowaste disposal in a class 3 landfill, the 1000°F cured, clay-containing foam (preferred) or the room temperature cured, non-clay-containing foam appear suitable as long as the landfill is not excessively alkaline. For excessively alkaline landfills, a 1000°F cured castable appears suitable. The recommended level of photowaste incorporation is 10-20% by weight of the green ceramic.

#### REFERENCES

1. R. E. Lotz, Chemical Wastes Generated by Air Force Photographic Operations, Air Force Weapons Lab., Kirtland AFB, New Mexico, September 1972, AD 750 552.
2. E. E. Lefebure and R. A. Callahan, Toxic Effects of Color Photographic Processing Wastes on Biological Systems, Environmental Health Lab., Kelly AFB, Texas, August 1970, AD 753 663.
3. What's Happening with Foamed Ceramics, Ceramic Age, November 1969.
4. J. Magder, Foamed Ceramics, U. S. Patent 3,330,675, July 1967.
5. R. W. Sicka, Foamed Ceramics, U. S. Patent 3,625,723, December 1971.
6. M. S. Vukasovich and H. L. Johns, U. S. Patent 3,148,996, September 1964.
7. H. H. Greger, Phosphate Cements, U. S. Patent 2,450,952.
8. H. H. Greger, Solid Aluminum Hydrogen Phosphates, U. S. Patent 2,538,867.
9. H. H. Greger, Method of Preparing a Mineral Binder, U. S. Patent 2,455,758.
10. W. D. Kingery, Fundamental Study of Phosphate Bonding in Refractories: I. Literature Review, J. of Amer. Ceramic Soc. 33, 239-241 (1950).
11. *ibid.* II. Cold-Setting Properties, *loc. cit.* 242-247 (1950).
12. *ibid.* III. Phosphate Adsorption by Clay and Bond Migration, *loc. cit.* 247-250 (1950).
13. *ibid.* IV. Motors Bonded with Monocaluminum and Monomagnesium Phosphate, J. Amer. Ceramic Soc. 35, 61-63 (1952).
14. I. L. Rashkovan, L. N. Kuzminskaya and V. A. Kopiekan, Thermal Transformations in the Aluminum Phosphate Binding Agent, Izvestiya Akademii Nauk SSR, Noerg. Materialy 2, pg. 541-549 (1966).
15. V. M. Medvedeva, A. A. Medvedev, and I. V. Tananaev, Investigation of the Thermal Transformations in An Alumina-phosphate Binder by the Methods of Infrared and X-Ray Diffraction Study, Izvestiya Akademii Nauk SSR, Noerg. Materialy 1, pg. 211-217 (1965).



References (continued)

16. Ya. V. Khyacharev and L. I. Skoblo, Composition of the Products Formed by the Hardening of Aluminum Phosphate Binder in Refractory Corundum Compositions, *Zhurnal Prikladnoi Khimii* 38, pg. 520-526 (1965).
17. M. F. D'Yvoire, Sur des phosphates d'aluminum du groupe  $P_2O_5/Al_2O_3 = 2$ , *Compt. rend.* 247, 297-300 (1958).  
  
M. F. D'Yvoire, Evolution thermique de phosphate d'aluminum du groupe  $P_2O_5/Al_2O_3 = 3$ , *Compt. rend.* 245, 531-534 (1957).  
  
M. F. D'Yvoire, *Bull. Soc. Chim. France* 145, 2277, 2283 (1960).
18. W. R. Beck, Crystallographic Inversions of the Aluminum Orthophosphate Polymorphs and Their Relation to Silica, *J. Amer. Cer. Soc.* 32, pg. 147 (1949).
19. K. Wen-min, N. Tchang-ti- and H. Wenter, Phase Transformation of Aluminum Phosphate Adhesive at 105-500°C, *Guisuanyan Xuebao*, pg. 65 (1964) CA 61:15808.
20. G. Yamaguichi and Y. Kubo, Ultramarine Synthesized Under Controlled Vapor Pressures, *Bull. Chem. Soc. of Japan*, 41, 2645 (1968).
21. R. Van Order and R. H. Hill, Manufacture of Ultramarine Blue, U. S. Patent 2,806,802.
22. W. J. Kruppa, et al., Manufacture of Ultramarine, U. S. Patent 2,700,618.
23. E. W. Large, Ultramarine Blue, *Am. Perfumes Cosmet.* 77 (91 422-44 (1962)).
24. F. Moser, Ultramarine Pigments, pg. 409, *Pigment Handbook Vol. I*, ed. T. C. Patton, J. Wiley & Sons, Inc. (1973).
25. J. T. Morrison, Ultramarine Pigments, *Paint and Varnish Prod.*, 61 pg. 59-64 (August 1971).
26. Ultramarine Blue, ASTM D262-47.